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VAPOR-LIQUID EQUILIBRIUM IN THE
NITROGEN-METHANE-N-HEXANE SYSTEM

BY



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A THESIS

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ABSTRACT

UNIVERSITY OF ALBERTA

A study FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Vapor-Liquid Equilibrium in the Nitrogen-Methane-n-Hexane System" submitted by H.H. Hamza in partial fulfilment of the requirements for the degree of Master of Science.

ABSTRACT

A study of the vapor-liquid phase equilibrium for the system Nitrogen-Methane-n-Hexane was made at temperatures of 40° and 100°F and pressures of 500, 1,000 and 2,000 psia.

A variable volume, windowed equilibrium cell, with mercury as the confining liquid was used in this work. The experimental and analytical equipment and techniques used are described.

The analyses of the equilibrium phases at the different conditions of temperature and pressure are presented. The equilibrium ratios were calculated using the experimental data and were compared with those calculated using the Winn Nomograph and the NGPSA Engineering Data Book. It was found that these methods do not give a good prediction of the K-factors, probably because of the difficulty in making a reliable calculation of the convergence pressure at the temperatures investigated for this system.

The Chueh-Prausnitz method was used to predict the critical loci of the Nitrogen-n-Hexane and Methane-n-Hexane systems. For this last system, no critical experimental data were used in the prediction, but the calculated locus compared very closely with that experimentally obtained.

The Chueh-Prausnitz method was used to calculate the bubble point temperature and vapor composition from a

knowledge of the pressure and liquid composition for the Nitrogen-Methane-n-Hexane, Nitrogen-n-Hexane and Methane-n-Hexane systems. When compared with the experimental results, it was found that the prediction of the bubble point temperature and vapor composition were not accurate. The binary data needed for the calculation had to be obtained by extrapolation, and it is believed that the available data were insufficient. It was concluded that before reliable calculations could be made using this method, experimental information on the binary pairs must be available over the entire temperature range.

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I INTRODUCTION

The vapor-liquid equilibrium behavior of hydrocarbon and hydrocarbon-non-hydrocarbon systems is of great practical and theoretical importance.

The properties of coexisting phases are needed for the proper design and operation of industrial equipment encountered in the chemical-petroleum processing field such as distillation columns, absorbers and evaporators.

Experimental and theoretical methods are now used to describe the properties of the equilibrium phases in hydrocarbons and related systems by specifying the equilibrium ratios of the components. The theoretical methods used are either thermodynamically or empirically developed. Assumptions made during the formulation of those methods limit the range of their application.

The vapor-liquid equilibrium of many hydrocarbon-non-hydrocarbon systems have been investigated, but there are still many systems of practical and theoretical interests that have not yet been studied. The prediction of the equilibrium ratios for these systems has recently been facilitated and improved by means of newly developed methods such as the Chueh-Prausnitz method. This method has the advantage that the effect of the composition on the activity coefficient of the liquid is calculated separately from the effect of the pressure and that only

properties of pure components and binary pairs are needed for the prediction of ternary and multicomponent phase behavior.

The fact that nitrogen is present in appreciable amounts in petroleum reservoirs, made the study of the phase behavior of nitrogen with hydrocarbon systems very important for the production and processing of the petroleum fluids. As long as thirty years ago, Boomer and Johnson, at the University of Alberta, realized the importance of the non hydrocarbon-hydrocarbon systems. They originated the study of the effect of nitrogen on hydrocarbon systems by investigating the vapor-liquid equilibrium of the following systems: Nitrogen-Methane-n-Pentane, Nitrogen-Methane-(n+iso)-Pentane, Nitrogen-Methane-n-Hexane, Nitrogen-Methane-(n+iso)Hexane, Nitrogen-Methane-n-Heptane. They used a gas composed of 5.6% nitrogen and 94.4% methane, and studied the Nitrogen-Methane-n-Hexane system in the range of temperature from 25°C to 85°C, and the pressure from 35 to 230 atm.

It was only recently, that Poston and McKetta, studied the same system at temperatures from 100 to 340°F and pressures from 500 to 5,000 psia.

For this work, it was decided to continue the study of the Nitrogen-Methane-n-Hexane system at a temperature of 40°F and at pressures up to 2,000 psia.

The objectives of this study were

1. To extend the range of temperature over which K-factors were available for the Nitrogen-Methane-n-Hexane system.
2. To compare the K-factors obtained by other methods like the NGPSA and the Winn Nomograph, at the high convergence pressure caused by the presence of nitrogen.
3. To try to reach a conclusion about the best method available for the prediction of the K-factors and improve the prediction if possible.

II THEORY

The Phase Rule

The phase rule given in 1876 by J. Willard Gibbs is still frequently used in phase behavior studies. It makes it possible to calculate the number of variables that have to be specified in order to completely define a system at equilibrium. It can be mathematically expressed as follows:

$$F = C - P + 2 \quad (1)$$

where F = the number of degrees of freedom of the system

C = the number of components of the system

P = the number of phases in equilibrium in the system.

Therefore in a three component system, when a state of equilibrium exists between two phases, three independent variables have to be specified in order to completely describe the system.

Criterion of Equilibrium

The necessary conditions for equilibrium to exist between any mixture of components in the vapor and liquid phases are

$$T^V = T^L \quad (2)$$

$$P^V = P^L \quad (3)$$

$$\bar{f}_i^V = \bar{f}_i^L \quad (4)$$

where T^V , T^L are the temperatures of the vapor and liquid phases
 P^V , P^L are the total pressures of the vapor and liquid phases
 \bar{f}_i^V , \bar{f}_i^L are the fugacities of component i in the vapor and liquid phases.

Equilibrium Ratio

The equilibrium phase distribution ratio or K-factor is the most common equilibrium quantity used in process calculations for coexisting vapor-liquid mixtures. It is arbitrarily defined as

$$K_i = \frac{Y_i}{X_i} \quad (5)$$

where Y_i and X_i are the mole fractions of component i in the vapor and liquid phases.

Several texts (45, 46, 22, 16) have dealt with the thermodynamics of phase equilibria at high pressures. These books have included detailed discussions on the different methods available for predicting the equilibrium ratio for hydrocarbon and other components of interest to the petroleum industry. No method is completely general; every method involves certain assumptions which make it applicable over a limited range.

Ideal Equilibrium Ratios

At low pressure, the fugacity can be replaced by the pressure and the criteria of equilibrium could be taken as

$$\bar{p}_i^V = \bar{p}_i^L \quad (6)$$

where \bar{p}_i^V and \bar{p}_i^L are the partial pressures exerted by component i in the vapor and liquid phases.

Assuming that the coexisting vapor and liquid phases are both ideal solutions, that the vapor phase behaves as an ideal gas, and that the vapor pressure of the liquid is a function of temperature and is not affected by the pressure; then a combination of Raoult's and Dalton's law could be used to calculate the equilibrium ratio

$$\bar{p}_i^L = x_i P_i^O \quad \text{Raoult's law} \quad (7)$$

$$\bar{p}_i^V = y_i P \quad \text{Dalton's law} \quad (8)$$

$$\text{At equilibrium } K_i = \frac{y_i}{x_i} = \frac{P_i^O}{P} \quad (9)$$

where P_i^O is the vapor pressure of component i at the temperature of the system and P is the total pressure of the system.

Generally speaking, K -factors predicted by this method are restricted to low pressures, far below the critical.

Ideal Solution Equilibrium Ratios

To eliminate the assumption made in Dalton's law of ideality in the vapor phase, the fugacity could then be used instead of pressures. With the assumptions that the liquid and vapor phases are both ideal solutions, the Lewis-Randall fugacity rule could be applied

$$\bar{f}_i^L = x_i f_i^L \quad (10)$$

$$\bar{f}_i^V = y_i f_i^V \quad (11)$$

where f_i^L is the fugacity of component i as a liquid at the pressure and temperature of the equilibrium f_i^V is the fugacity of component i as a vapor at the pressure and temperature of the equilibrium.

Many methods have been reported to calculate the ideal solution equilibrium ratio. The ideal solution equilibrium ratio is only a function of the temperature and pressure of the system and does not depend on the composition.

The fugacity of either the liquids or vapors are sometimes obtained by extrapolation of the fugacity pressure relation to a hypothetical state. The ideal equilibrium ratio could also be calculated using an equation of state that represents the PVT behavior of the components in both the liquid and the vapor phases of the system. It has been found that the equilibrium ratios

obtained from the ideal solution theory do not hold as the critical conditions are approached.

Actual Equilibrium Ratios

The substitution of the activity for mole fraction in the equations derived for an ideal system, made those equations valid for real systems

$$\bar{f}_i^L = \gamma_i^L X_i f_i^L \quad (12)$$

$$\bar{f}_i^V = \gamma_i^V Y_i f_i^V \quad (13)$$

where γ_i^L and γ_i^V are the activity coefficient of component i in the liquid and vapor phases respectively at the system temperature and pressure.

Therefore, all the deviations from ideal behavior are corrected by the introduction of the activity coefficient which changes with temperature, pressure and composition. At equilibrium

$$K_i = \frac{Y_i}{X_i} = \frac{\gamma_i^L f_i^L}{\gamma_i^V f_i^V} = \frac{\gamma_i^L}{\gamma_i^V} K_{ideal} \quad (14)$$

There are no assumptions involved in formulating this equation but the difficulty is in finding a general method for calculating the activity coefficients.

Convergence Pressure

From the experimental results obtained for different systems, it was observed that the K-factors converge

to unity at some pressure for each temperature chosen. This pressure is called the convergence pressure.

The convergence pressure of a system is thus defined as that pressure for which the K-factors of all components in the system converge to unity at the system temperature.

Hanson and Brown (23) showed that for paraffin hydrocarbon systems that for a given component, the equilibrium ratios are the same for the same convergence pressure, even when the composition of the system is different.

The convergence pressure has been widely used as a composition parameter, to relate K-factors to the composition of the hydrocarbon systems.

When applying the phase rule to a two phase system, the number of degrees of freedom is equal to the number of components. If the convergence pressure is expressed as a function of temperature and N-2 composition parameters, the system will be completely described by fixing the pressure and the convergence pressure, then

$$K = f''(P, P_K) \quad (15)$$

For a binary system, the convergence pressure depends on the temperature alone, and is equal to the critical pressure of the system that has the equilibrium temperature for its critical temperature.

Several methods have been suggested for the prediction of the convergence pressure of multicomponent systems, and for the calculation of the equilibrium ratio using the convergence pressure concept.

Hadden (20) showed that the convergence pressure is a function of liquid phase composition excluding the concentration of the lightest component. He suggested the use of a composition parameter based on mass fraction to obtain the convergence pressure. For a ternary system, the composition parameter would be

$$M_2 = \frac{m_2}{m_2 + m_3} \quad (16)$$

where the components are numbered in the order of decreasing volatility.

m_2 = mass fraction of component 2 in the liquid phase

m_3 = mass fraction of component 3 in the liquid phase

Using the composition parameter suggested by Hadden, Winn (78) developed an expression for the convergence pressure of a ternary mixture as follows

$$P_k = \frac{m_2 P_2 + m_3 P_3}{m_2 + m_3} \quad (17)$$

P_2 and P_3 are the convergence pressures for the binaries

composed of components (1, 2) and (1, 3) respectively at the system temperature.

If the system temperature is greater than the critical temperature of component 2, then P_2 is taken equal to the critical pressure for component 2.

P_k is the convergence pressure for the ternary mixture at the specified values of M_2 and at the temperature of the system.

He presented a nomograph to obtain the K-factors when the convergence pressure was 5,000 psia. K-factors could be estimated when the convergence pressure was other than 5,000 psia, using a grid pressure evaluated from another chart.

Rzasa et al (56) devised a correlation to estimate the convergence pressure of complex hydrocarbon systems. They based their correlation on the relationship of the critical pressure of the system and the product of the molecular weight and specific gravity of the heptanes plus fractions. The obtained convergence pressures are then used to get the equilibrium ratios.

Hadden and Grayson (21) extended the Winn nomograph to obtain the equilibrium ratios at temperatures from -260°F to 800°F and at pressures up to 10,000 psia. These nomographs apply to light hydrocarbons and petroleum fractions and to certain non-hydrocarbon systems. Nitrogen is included in those nomographs. The K-factors are related to

component temperature, pressure and convergence pressure.

Myers and Lenoir (35) presented a nomograph to evaluate the K-factors using the value of K at 10 psia and a convergence pressure of 5,000 psia.

The values of the equilibrium ratios are increasingly affected by the convergence pressure when the operating pressure approaches the convergence pressure. Therefore, the convergence pressure should be accurately calculated to get a proper estimate of the equilibrium ratio.

The convergence pressure methods are the most widely used empirical methods to obtain the K-factor.

Chao-Seader

Chao and Seader (11) developed a correlation of vapor liquid equilibria in hydrocarbon mixtures. They calculated the equilibrium ratio for the components in the equilibrium mixture using a three parameter equation

$$\begin{aligned}
 K_i &= \frac{Y_i}{X_i} = \frac{\bar{f}_i^L / X_i}{\bar{f}_i^V / Y_i} \cdot \frac{P}{\bar{P}} \cdot \left(\frac{f_i^L}{f_i^L} \right) \\
 &= \frac{\bar{f}_i^L / f_i^L \cdot X_i}{\bar{f}_i^V / P \cdot Y_i} \cdot \left(\frac{f_i^L}{\bar{P}} \right)_i \\
 &= \frac{\gamma_i^L \cdot v_i^L}{\phi_i^V}
 \end{aligned} \tag{18}$$

where γ_i^L is the activity coefficient of component i in the liquid solution
 v_i^L is the fugacity coefficient of pure liquid component i at the conditions of the system
 ϕ_i^V is the fugacity coefficient of the component i in the vapor mixture.

The Redlich-Kwong equation of state was used for the calculation of the fugacity coefficient of component i in the vapor mixture. To apply the equation, two constants are required for every component, these are directly related to the critical temperature and pressure.

Chao and Seader calculated the activity coefficient in the liquid with the assumption that the liquid hydrocarbon solutions are regular solutions. Regular solutions have their excess entropy equal to zero, any non-ideal behavior is due to the heat of solution. They used the equation given by Hildebrand

$$\ln \gamma_i = \frac{v_i (\delta_i - \bar{\delta})^2}{RT} \quad (19)$$

where v_i is the liquid molar volume of component i
 δ_i is the solubility parameter of component i

The solubility parameter is equal to the square root of an energy density i.e.

$$\delta = \left(\frac{\Delta E_V}{V} \right)^{1/2} \quad (20)$$

where ΔE_v is the energy of vaporization

$$\bar{\delta} = \frac{\sum_i X_i V_i \delta_i}{\sum_i X_i V_i} \quad (21)$$

The solubility parameter and molal volume could be taken as functions of temperature. However, it was found that they could be considered as characteristic constants of a component without appreciable loss of accuracy.

The liquid fugacity coefficient of pure components have been correlated with a modified form of the principle of corresponding states given by Pitzer.

Accordingly

$$\log v^o = \log v^{(0)} + \omega \log v^{(1)} \quad (22)$$

$v^{(0)}$ and $v^{(1)}$ have been fitted with approximating functions and depend only on reduced temperature and reduced pressure.

ω is the acentric factor, it gives a measure of the deviation of the behavior of usual substances from that of an idealized simple fluid. It is a characteristic constant for each component.

The Chao-Seader correlation can give high accuracy in the range specified below:

1. For hydrocarbon (except methane), a reduced temperature range from 0.5 to 1.3 based on the pure component critical

temperature and pressures up to 2,000 psia but not to exceed about 0.8 of the critical pressure of the system.

2. For systems containing light gases like hydrogen and methane

- a) The reduced temperature should not exceed 0.93
- b) The temperature lies between -100 F and 500 F
- c) Pressures up to 8,000 psia
- d) Other dissolved gases should be below 20 mole percent in the liquid.

Lenoir and Koppany (33) showed that for binary mixtures of methane in hexane and paraffin of higher molecular weight, the Chao-Seader method predicts the equilibrium ratio of the heavier paraffin very poorly.

Prausnitz (44) mentioned some limitations of the Chao-Seader correlation and stated that this correlation is unreliable at conditions approaching the critical.

Chueh-Prausnitz

Prausnitz and Chueh (45) presented equations for reducing binary vapor-liquid equilibrium data to thermodynamically significant binary parameters; upon generalizing these equations to systems containing any number of components, they were then able to predict the phase behavior of multicomponent mixtures. Their method is restricted to non-polar or slightly polar fluids as those encountered in the petroleum industries.

For the vapor-liquid equilibrium of an N-component system, there are N degrees of freedom.

For a system in equilibrium

$$\bar{f}_i^V = \bar{f}_i^L \quad (4)$$

where $i = 1, 2, 3, \dots$ to N

Prausnitz and Chueh made use of the following equations, to be able to solve the N simultaneous equations given by (4)

$$\bar{f}_i^V = \phi_i Y_i P \quad (23)$$

$$\bar{f}_i^L = \gamma_i^{(P)} X_i f_i^{\circ(P^r)} \quad (24)$$

$$\gamma_i^{(P^r)} = \gamma_i^{(P)} \exp \int_P^{P^r} \frac{\bar{v}_i}{RT} dP \quad (25)$$

where ϕ_i is the fugacity coefficient of component i in the gas mixture

P is the total pressure of the system

$f_i^{\circ(P^r)}$ For the solvents, it is the fugacity of pure liquid i at the temperature of the solution and at the constant reference pressure P^r .

For the solutes, it is Henry's constant for the solute i in the solute-free solvent mixture at system temperature and at the constant reference pressure P^r .

$\gamma_i^{(P)}$ is the activity coefficient for component i
at P

$\gamma_i^{(P^r)}$ is the activity coefficient for component i
at the reference pressure P^r

P^r Standard State Pressure

\bar{v}_i Partial molal volume of component i in the
liquid mixture.

The simultaneous solution of the equations given by (4)
is most conveniently performed by an iterative procedure.
The solution must satisfy the two stoichiometric relations

$$\sum_{i=1}^N X_i = 1$$

and
$$\sum_{i=1}^N Y_i = 1$$

A thermodynamic description of high pressure vapor-
liquid equilibrium must describe how the fugacity of each
component, in each phase, depends on the temperature,
pressure and composition.

In the vapor phase, this dependence is given by the
fugacity coefficient, and in the liquid phase, this de-
pendence is determined essentially by the effect of tem-
perature, pressure and composition on the activity coeffi-
cient.

It is necessary then to calculate the fugacity co-
efficients, the activity coefficients, the reference

fugacities and the partial molar volumes.

ϕ_i was calculated as a function of (P, T, Y_i) using a revised Redlich-Kwong equation of state (to take into account the deviations from the geometric mean approximation) with new mixing rules.

P^r the standard State pressure was taken for convenience equal to 0

$f_i^{(P^r)}$ It is an experimentally accessible quantity

\bar{v}_i was calculated in terms of T, X_i and the saturated liquid molar volume of the mixture. The Redlich-Kwong equations of state was applied to fit the PVT data of saturated liquid for each pure component. Modified mixing rules were used to apply the equation to the liquid mixture using corresponding states correlation.

The symmetric convention of normalization was used for the activity coefficients of solvents, and the unsymmetric normalization was used for solutes.

$\gamma_i^{(P^r)}$ was calculated as a function of T and X_i using a two parameter equation obtained from a dilated van Laar model. To obtain the constants of the equation, self-interaction and dilation constants are needed, those are obtained from binary data. The van Laar's equation was modified to allow for the rapid change of the liquid molar volume which occurs in the critical region.

The method can be used to calculate multicomponent

vapor-liquid equilibria for non-polar or slightly polar systems, but in addition to the pure component properties some binary data for all possible binary pairs in the mixture are needed.

The method has not yet been extensively tested in practice but it is considered to be one of the best proposals to date for predicting vapor-liquid equilibrium at high pressure.

III RELATED SYSTEMS INVESTIGATED

The properties of pure nitrogen and pure methane have been extensively studied and are well established. Less work has been done with n-hexane. The properties of n-hexane at atmospheric pressure have been studied in some detail and were summarized by Rossini (55). The earlier work of Shepard (67) served to establish the index of refraction and the specific weight at atmospheric pressure which was also evaluated by Wibaut (76, 77). Kelso and Felsing (27, 28) studied the volume-temperature relations of n-hexane at pressures up to 4,500 psia, and Eduljee and co-workers (17) determined the volumetric behavior of this compound at pressures up to 75,000 psia. Stewart, Sage and Lacey (71) investigated the volumetric behavior of n-hexane at pressures up to 10,000 psia and temperatures between 100° and 460°F. Leverett (34) determined the PVT properties of n-hexane at 200-800 mm Hg and 40°-200°C.

Related Nitrogen Binary Systems

The vapor-liquid equilibrium of the nitrogen-methane system has been studied by several investigators (9, 13, 74, 36, 18). McTaggart and Edwards (36) studied this system at atmospheric pressure and their results show large deviations from ideal solution behavior. Torochesnikov and Levins (77) determined six isotherms for the nitrogen-

methane system between -298° and -200°F , while Cines et al (13) made their investigation in the temperature range of -280°F and -150°F . Bloomer and Parent (7) studying the same system, covered the range of pressure from atmospheric through the critical region. The lowest temperature they studied was -295°F , and the highest was the critical temperature of methane -116.7°F . They reported some experimental values for the densities of the saturated liquid and saturated vapor phases of pure methane, and were able to draw the critical locus curve. The agreement was in general excellent between the data reported by Bloomer and Parent, and Cines et al. The greatest difference was in the critical region. The data of Bloomer and Parent, and Cines et al, do not agree with the earlier data reported by Torocheshinkov and Levins.

Akers, Attwell and Robinson (1) investigated the vapor-liquid equilibrium of the nitrogen-butane system at temperatures from 100° to 300°F . From their results, a retrograde region was found, and the K-factors for the nitrogen decreased rapidly as the temperature was increased by increasing the temperature. They have drawn the critical locus over the range of data taken. They used the Edwards gas density balance to get the composition of their phases. Roberts and McKetta (53) reported data that considerably disagree with the results of Akers et al. They attributed the inaccuracy in the results of Akers and

co-workers to the extreme sensitivity required when analyzing the phases with the density balance. Their study was conducted in the temperature range from 100° to 280°F and a pressure from 236 to 3402 psia.

Poston and McKetta (42) experimentally determined the vapor-liquid equilibrium compositions for the nitrogen-n-hexane system over a pressure range from 250 to 5,000 psia and at temperatures from 100° to 340°F. They found like other investigators (1, 5, 53) that the solubility of nitrogen in the liquid hydrocarbon phase increases with pressure.

Boomer, Johnson and Piercy (10) obtained the solubility and phase density data of nitrogen in n-heptane at 100.9 atmosphere and temperatures from 25° to 115°C. Akers, Kehn and Kilgore (3) reported the volumetric and phase behavior of the same system at temperatures between 90° and 360°F. They found that at 90°F the density of the liquid phase increases with the increase of pressure. At higher temperatures, the greater solubility of the nitrogen in heptane causes the density to decrease with increasing pressure. They attributed this unusual phenomenon to the non-ideality of the nitrogen-heptane solutions.

Related Methane Binary Systems

The methane-ethane system has been studied by some investigators (22). Price and Kobayashi (47) in their study of the vapor-liquid equilibrium of the methane-

ethane-pentane system reported their results of the binaries methane-ethane and methane-propane systems in the temperature range of -200°F to 50°F and the pressure from 100 to 1400 psia. No azeotropic mixtures were found in this range.

Sage, Lacey and Schaafsma (57) studied the methane-propane system and determined the densities of different mixtures in the pressure range of 10 to 200 atm. and temperatures from 20° to 90°C ; the vapor-liquid equilibrium compositions were reported at pressures from 10 atm to 95 atm, and temperatures from 20° to 90°C . They obtained a large region of retrograde condensation of the first kind. Reamer, Sage and Lacey (49) extended the range of study to a pressure up to 10,000 psia and temperatures from 40° to 460°F , while Akers, Burns and Fairchild (2) investigated the methane-propane system at temperatures from -176° to 32°F and pressures from 50 to 1,450 psia. They drew the phase envelopes for various mixtures. Their data are in agreement with the results obtained by Sage, Lacey and Schaafsma.

Neberbragt (38) in his study of the vapor-liquid equilibrium of the methane-butane system used n-butane containing a small percentage of iso-butane (96.6% n-butane and 3.4% iso-butane). He studied this system at pressures of 10 to 30 atm. and temperatures from -21° to 43°C . Sage, Hicks and Lacey (61) reported the

compositions and specific volumes of the coexisting phases of the methane-n butane system from 70° to 250°F and 31.3 to 1923 psia. They showed the loci of the critical states and the cricondentherm. Roberts et al (54) extended the range of study from -80° to 280°F, their data are in agreement with Sage et al. Wang and McKetta (75) reported the vapor-liquid equilibrium data of the same system at -140°F and pressures from 73 to 453 psia.

Sage, Webster and Lacey (62) studied the solubility of methane in n-pentane at 100°, 160° and 220°F at pressures up to 3000 psia. They found that the solubility of methane in pentane increases rapidly at high pressures. Boomer, Johnson and Piercy (8) determined the densities and compositions of the equilibrium phases of the n-pentane-methane system at 25°, 55° and 85°C at total pressures from 35 to 190 atm. Similar measurements at 25°C and pressures from 35 to 135 atm. were made on a system composed of a mixture of n-pentane and iso-pentane with methane. The work of Sage and co-workers was found to agree with the work of Boomer et al., but a regular small discrepancy appeared which could be attributed to the presence of a small percentage of nitrogen in the gas used by Boomer and co-workers. Boomer et al found that methane is more soluble in the mixture of pentanes than in pentane alone; this is also in agreement with Hill and Lacey. Taylor et al (73) reported the phase behavior of

the methane-n pentane system through the temperature range of 100° to 220°F. Their results indicate a progressive decrease in the critical pressure of this system with an increase in temperature, and a rapid change in the composition of the dew point gas with pressure at the low pressure. Sage et al (60) determined the specific volume of six mixtures of methane and n-pentane for temperatures between 100° and 460°F, at pressures up to 5,000 psia. They reported the compositions of the coexisting phases at equilibrium as well as the equilibrium constants. They drew the loci of the cricondentherm, the critical state and the maximum two-phase pressure.

Several investigators (41, 9, 19, 62, 66, 68, 70, 24, 69) have studied the vapor-liquid equilibrium of the methane-n hexane system. Frolich et al (19) measured the solubility of methane in n-hexane at 25°C and at pressures as high as 1,300 psia, they found that the solubility of methane in normal hexane followed Henry's law fairly closely. Hill and Lacey (24) determined the solubility of methane in hexane at 86°F and 300 psia, while Sage, Webster and Lacey (62) went up to a pressure as high as 2,500 psia and temperature from 100° to 220°F. Their results, if interpolated to 25°C, will be lower than those reported by Frolich et al (19). Bubble point and dew point densities and compositions at 25°, 55° and 85°C corresponding to pressures up to 230 atm., were reported by Boomer and Johnson (9) for the methane-n

hexane mixtures which contained a small amount of nitrogen. The data reported by Boomer and co-worker is in substantial agreement with that of Sage et al. Schooch, Hoffmann and Mayfield (66) determined the solubilities of methane in n-hexane at temperatures of 160° and 220°F and corresponding to pressures up to the critical. They showed that the maximum critical pressure exists at a temperature somewhere between 100° and 220°F. They also determined the densities and the compressibilities of the resultant solutions up to pressures of 6,000 psia. Stepanova and Vybornova (70) investigated the methane-n hexane system between 50 and 210 atm., and 0° and 60°C, they reported the critical pressure and equilibrium constants. Shim and Kohn (68) investigated the vapor-liquid equilibrium compositions of the methane-n hexane system at temperatures between -110° and 150°C and pressures up to 160 atm. They found that there is a gradual decrease in the solubility of methane in the liquid phase of the methane-light paraffin hydrocarbons, as the paraffin molecular weight increases. N-hexane is the highest molecular weight paraffin which is completely miscible with methane. The temperature range of 100° to 340°F and pressure range of 250 to 2,902 psia was covered by the study of Poston and McKetta (41). They showed that the solubility of methane in n-hexane decreases with temperature. Their data are in agreement with the data of

Boomer (9), Sage (62), Schooch (66) and Shim (68) except for the critical temperatures reported by Shim and the vapor compositions reported by Boomer. Small disagreement with Boomer's composition data was also reported by Shim. Poston's data agreed to within 0.5 mole percent with data interpolated from Shim.

Boomer, Johnson and Piercy (10) studied the methane-heptane system and reported the densities and compositions of both equilibrium phases at temperatures 25°, 55° and 85°C, and pressures from 35 to 250 atm. Reamer et al (48) conducted their volumetric and phase behavior studies at pressures up to 10,000 psia in the temperature interval between 40° and 460°F. He found that at a temperature lower than -114.7°F, two liquid phases exist which is unusual for paraffin hydrocarbon system. Kohn (29) made his study at pressures up to 1,500 psia and from -200° to 340°F. The results of Reamer when compared with those of Boomer showed a large difference; while an excellent agreement was obtained between the data of Reamer and that of Kohn.

Kohn and Bradish (30) determined the vapor-liquid compositions and molar volumes of the methane-n-octane system at eight different temperatures between -50° and 150°C. Temperatures, pressures and compositions along the three phase (vapor-liquid-solid) lines have been reported at temperatures between -107.6° and 56.7°C. They found that

Raoult's law does not hold accurately for n-octane past 0.20 mole fraction methane.

Sage, Lavender and Lacey (59) studied the volumetric behavior of several mixtures of methane-n-decane at pressures up to 4,500 psia and in the temperature interval between 70° and 250°F; the composition of the dew point gas was also determined at pressures up to 2,500 psia at 100°, 160° and 220°F. Reamer et al (50) in his study covered the range of pressure from 20 to 5,300 psia and temperatures from 100° to 400°F. Koonce and Kobayashi (31) experimentally determined the solubility of methane in n-decane from measurements of pressure, temperature, and volume only. They calculated the K-values from methane in the methane-n-decane mixture at temperatures between -20° and +40°F, on the assumption that the vapor is free from the non-volatile components. Their results are consistent with the work of Sage and Lacey (58) carried out at higher temperatures. Beaudoin and Kohn (6) studied the vapor-liquid equilibria of the methane-n-decane system at temperatures between -25° and 150°C; at pressures up to 100 atm. They found that Henry's law expressed as fugacity-mole fraction ratio holds as a reasonably accurate approximation at pressures below 30 atm.

Related Ternary Systems

Roberts and McKetta (51) experimentally determined the equilibrium compositions for the methane-n-butane-

nitrogen system between 100° and 280°F, and 500 and 3,000 psia. They found that at 100°F the K-values of methane decrease with increasing the nitrogen concentration at 500 psia, but this trend is reversed above 1,500 psia. This behavior was attributed to the difference in solubility of the methane and nitrogen in the liquid phase. As the temperature and pressure increase this difference becomes smaller and smaller, and the K-factors of methane increase with increasing concentrations of nitrogen at constant pressure.

Boomer et al (9, 8, 10) studied the vapor-liquid equilibrium of the nitrogen-methane-pentane, nitrogen-methane-hexane, nitrogen-methane-heptane systems at pressures from 35 to 250 atm. and in a temperature range from 25° to 85°C. They found that the behavior of the equilibrium constants is very similar for the three systems, with a regular variation from compound to compound. At all comparable pressures, the K-factor of the heavier hydrocarbon in the systems decreases when going from pentane to heptane, and changes most with temperature in the case of pentane. While the equilibrium constant for methane, at pressure above 50 atm. increases in going from pentane to heptane. The region of retrograde condensation is largest for heptane and least for pentane; and is reduced by increasing the temperature.

Azarnoosh (4) investigated the methane-n-decane-nitrogen system between 100° and 280°F, and 1,000 and

5,000 psia with the nitrogen concentration varying from 0% to 100% in the vapor phase. He found that the change in convergence pressure of this system is linear with the change of nitrogen concentration in the vapor phase since the mole fraction of n-decane in the vapor phase is extremely low. The convergence pressures at zero and one hundred percent nitrogen in the vapor phase are equal to the critical pressures of the binary systems of decane-methane and decane-nitrogen respectively at the same temperature. He found that as the mole fraction of nitrogen in the vapor phase increases, the K-factors of methane and nitrogen increase, while the K-factor of decane decreases.

Multicomponent Systems

Stutzman and Brown (72) experimentally determined the compositions of the vapor-liquid equilibrium phases for the common components of a natural gas including nitrogen and methane, at a total pressure of 100 psia and temperature which varied from -130° to 240°F . Davis et al (15) presented the phase and volumetric properties of some natural gases and mixtures of natural gases with methane and nitrogen from -200°F to above the critical points. Jacoby and Rzasa (26) determined the vapor-liquid equilibrium compositions for nitrogen, methane, carbon dioxide, ethane and hydrogen sulphide in a natural gas-

condensate system. Two different overall mixture compositions were investigated over the pressure range 500 to 4,000 psia at 100°, 150° and 200°F. Cosway and Katz (14) studied the systems containing hydrogen, nitrogen, methane and ethane at pressures of 500 and 1,000 psia and at temperatures of -100° and -200°F. They reported the compositions of the conjugate phases at equilibrium for three ternary and the quaternary systems. Lehigh and McKetta (32) reported the compositions of the conjugate equilibrium phases for the nitrogen-ethane-butane system at temperatures from 100° to 280°F and pressures from 500 psia to the convergence pressure.

Roberts and McKetta (52) studied the effect of nitrogen on the vapor-liquid equilibrium ratios of hydrocarbons in natural gas condensate system. Their experimental work was carried out under constant temperature conditions at 100°F and at 220°F, and at different pressures between 500 and 3,000 psia. The nitrogen concentration in the vapor phase was varied from 10% to 50% at each pressure. They found that the K-factors of the hydrocarbons were lowered by the addition of nitrogen and the effect was more pronounced at 220°F than at 100°F.

Nitrogen-methane-n hexane System

Poston and McKetta (43) studied the phase equilibria of the nitrogen-methane-n-hexane system at temperatures from 100° to 340°F and pressures from 500 to 5,000

psia. They found that at 100°F and low pressures (around 500 psia) the addition of nitrogen to the system at constant pressure causes methane to be preferentially dissolved in the liquid phase. The liquid phase at low pressures is composed principally of n-hexane. Therefore, methane at low pressures is more soluble in n-hexane than is nitrogen. However, at pressures of 1,000 psia or more some of the physical properties of methane and nitrogen approach one another and their solubilities in the liquid phase follow the same trend. Because of this the K-values of methane increase with the addition of nitrogen in the vapor phase.

IV EXPERIMENTAL STUDIES

1. Experimental Apparatus

(a) Equipment

A very detailed and complete description of the original design of the vapor-liquid equilibrium apparatus has been presented by Sandercock (63). The equilibrium cell used in these experiments was a 600 ml cylindrical, windowed cell of variable volume made of 316 stainless steel. It was designed to withstand a pressure of 8,000 psia at a maximum temperature of 300°F. The freezing point of mercury, the confining liquid, determined the minimum operating temperature. The cell was designed to contain three sections: a gas section with a floating piston, a restriction with a window assembly, and a liquid section having less capacity and smaller diameter than the gas section.

The position of the vapor-liquid interface in the cell could be changed without changing the volume of the equilibrium mixture. This was accomplished by connecting the top and bottom of the cell to two ends of a double acting pump and in this way mercury could be removed from one end at the same rate that it was added to the other end. Thus, the equilibrium mixture being confined between mercury and the movable piston, could be moved to the desired level. The displacement pump connected to the bottom of the cell

was used to add or withdraw mercury thus decreasing or increasing the working volume of the cell.

In order to see the inside of the cell around the sampling port, a periscope arrangement was used. Light was provided through a 1 in. by 1 in. "bull's eye" type of window and viewed through a telescope adjacent to the opposite window.

Mixing of the cell mixture was done by spraying the liquid phase and some mercury into the vapor phase using the double acting pump. A valve, placed in the lower section of the cell, and having a small aperture provided a fine spray of the fluids (65).

Charging and sampling were done through a port at the window level. Samples were taken by means of a micrometer sample pump, having a total volume of about two cubic centimeters. In the original design, the sample pump was placed horizontally, but later (64) it was changed by a new pump placed vertically to prevent the possibility of a slug of the sample fluid being trapped in the pump.

The cell and sample pump were immersed in separate ethylene glycol constant temperature baths. The pump was usually maintained at a higher temperature than the cell to avoid condensation of n-hexane during sampling. A bimetallic strip-controller was placed in an auxiliary bath, and used to govern the heater and refrigeration units giving a constant temperature for the ethylene glycol cell bath.

A schematic arrangement of the experimental equipment is shown in Figure 1.

The temperature of the cell was measured using an iron-constantan thermocouple inserted into the side of the cell. The thermocouple was calibrated in the temperature range from 32° to 200°F, against a standard precision mercury thermometer readable to 0.05°C, and a millivolt potentiometer, model 8686 manufactured by Leeds and Northrup Company, was used to measure the potential. The temperature was controlled to within $\pm 0.3^\circ\text{F}$ and read to within $\pm 0.1^\circ\text{F}$. The pressure of the system was measured using two Heise Bourdon gauges rated at 5,000 psia and 1,000 psia and marked at intervals of 10 psi and 2 psi respectively. Both gauges were calibrated with a Ruska dead weight tester. The pressure was adjusted manually within ± 0.5 psi up to 1,000 psia and to within ± 3 psi above that.

(b) Leak Detection

The equipment used for the study of the vapor-liquid equilibrium at high pressure must be completely free from leaks. As a first step in the experimental program, therefore, the equipment was pressure tested, and all leaks were carefully eliminated. Leaking connections and valves were tightened or replaced. Studies including hydrogen sulphide had previously been conducted with the same equipment. This resulted in the deposition of mercuric sulphide on several parts including the valves, the pistons and cylinders of the pumps, and the windows, pistons and walls of

the cell. Several attempts were made to remove these deposits and it was finally found that sodium sulphide (39) was the most effective cleanser.

In the course of the experimental program, this equilibrium equipment was used at working pressures as high as 2,000 psia. Although when pressure tested, the equipment could hold a pressure of 2,500 psia for several hours, many leaks appeared during the experimental runs. Most of the leaks in the cell were around the windows, due to flowing or breaking of the gaskets. It was concluded that the gaskets suggested by Sandercock (63) and successfully used at pressures of about 1,500 psia, were not suitable. Gaskets made of a harder material had to be used and after several trial and error procedures it was found that glass-filled teflon was a suitable material.

Before starting the experiments, the sampling system was tested for leaks with a Veeco Mass Spectrometer Helium Leak Detector, Model MS-12AB-R. All leaks were eliminated. However, during the experimental work many leaks occurred in the sampling pump, most of them were at the packing, due to the flowing of the teflon packing rings suggested previously (64). The pump operated for a much longer period with no leaks at the packing when gaskets made of teflon and similar to Chevron packing rings were used.

DP DISPLACEMENT PUMP
 HG HEISE GAUGE
 DAP DOUBLE ACTING PUMP
 SP SAMPLING PUMP
 SB SAMPLING BOMB
 EC EQUILIBRIUM CELL
 V VACUUM
 MR MERCURY RESERVOIR

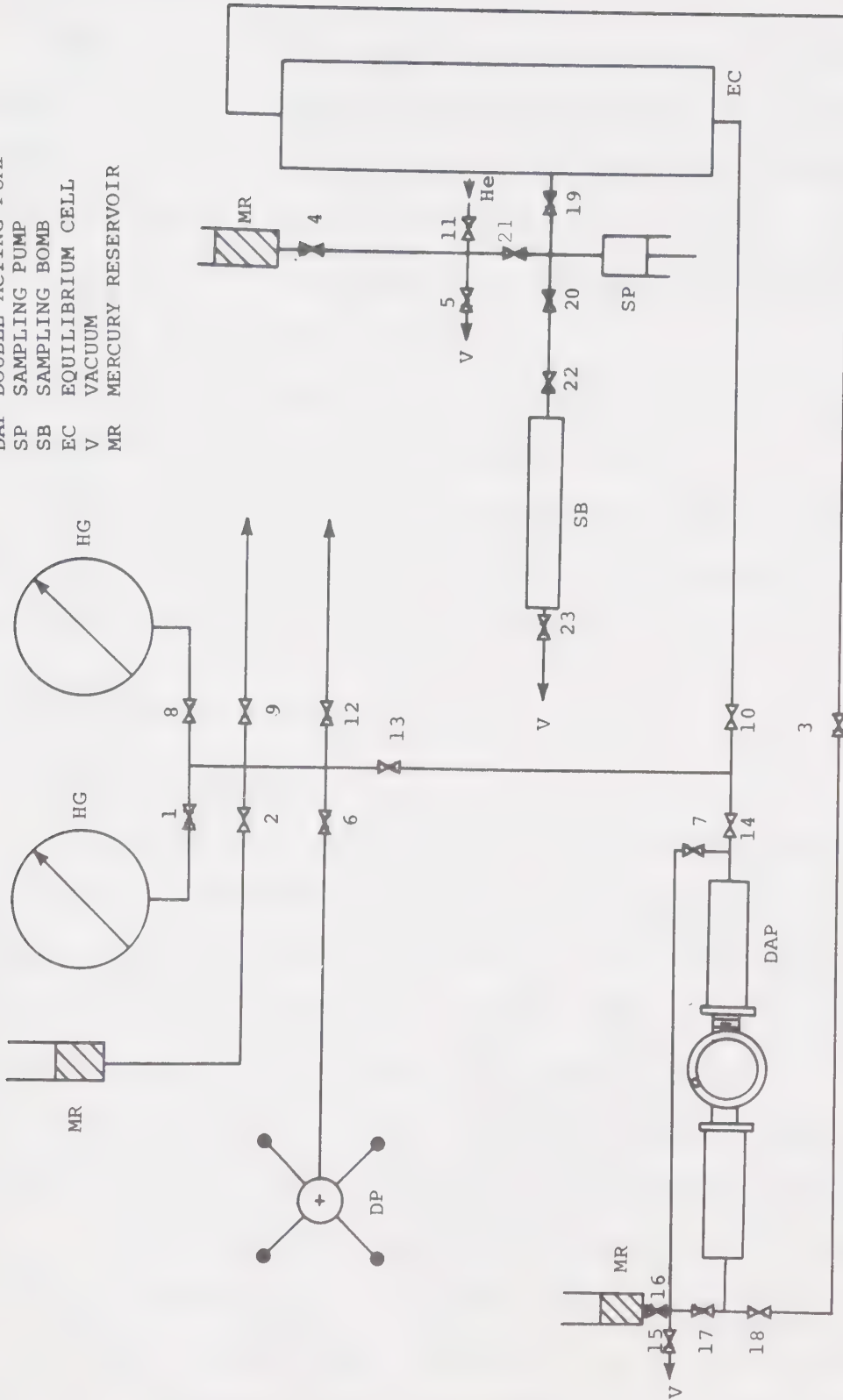


FIG. -1- EQUILIBRIUM EQUIPMENT

2. Materials Used

The normal hexane used in the experiment was Philipps Petroleum Company research grade n-hexane with a purity of 99.99 mole per cent. The impurity determined by GLC analysis was methyl cyclopentane. Matheson of Canada supplied the research grade methane which had a purity of 99.97 mole per cent.

Nitrogen was supplied by Canadian Liquid Air and had a minimum purity of 99.7 mole per cent.

Clean triple distilled mercury was used. The procedure used to clean the mercury has been detailed by Hughes (25).

3. Experimental Method

Charging the Cell

The equilibrium apparatus was first evacuated overnight and then completely filled with mercury and pressure tested. To charge the equilibrium cell with the three components, hexane, having the lowest vapor pressure, was introduced first, then methane and finally nitrogen. Hexane was charged to the cell either by means of the sampling pump, or it was allowed to flow freely into the cell. In the latter case, some nitrogen was first introduced at the sampling port and some mercury was removed from the bottom of the cell, vacuum was then applied to evacuate the nitrogen, while the piston was at its lowest

position in the cell. Hexane was then admitted. The gases were charged to the cell by connecting the cylinder containing the gas to the sampling pump. The lines connecting the cylinder, pump and cell were evacuated; the gas was then allowed to enter the cell. When the pressure in the cell was equal to the pressure in the gas cylinder, the displacement pump could then be used to introduce more gas by removing some mercury from the bottom of the cell.

Attainment of Equilibrium

After the cell had been charged and contained the three components in two phases, the temperature and pressure were adjusted to the working conditions. The double acting pump was used to lower the liquid level below the internal valve. The double acting pump was then actuated rapidly enough to push the liquid through the internal valve, thus producing a fine spray into the vapor phase. This produced mixing of the phases and a change in pressure was noticed when the phases were not in equilibrium. The displacement pump was then used to adjust the pressure in the cell. The phases were allowed to separate and the mixing procedure was repeated until the pressure stabilized. The contents of the equilibrium cell were allowed to stand undisturbed for a period of two to four hours for the phases to completely separate. The liquid and then the vapor were sampled and analyzed.

Sampling Techniques

The solution of the problems encountered in sampling the equilibrium fluids required considerable thought and experimentation. The aim of sampling is to transfer a small representative sample of the equilibrium phases from the cell to the chromatograph to be analyzed.

The sample must represent accurately the composition of the phases in the equilibrium cell and they must be in the vapor phase while being injected into the chromatograph. The method used was to transfer a small sample at high pressure from the equilibrium cell to the sampling pump, then expand this sample into an evacuated container. A portion of the expanded sample was then injected into the chromatograph.

(a) Sampling Procedure

Referring to Figure 1, the sampling procedure may be stated as follows:

1. The sampling lines, pump and container were first evacuated with valves number 5, 21, 23 and 22 completely open, and numbers 19, 20, 11 and 4 closed.
2. The vacuum system was closed off at 5.
3. Valve 4 was then cautiously opened and mercury allowed to fill the tubing between valves 4 and 19. Some mercury was allowed into the sampling pump while the phase to be analyzed was at the window level in the cell.

4. Valve 21 was then closed, and valve 19 opened while mercury was slowly pushed into the cell by the sampling pump.
5. When the first droplet of mercury was observed through the window, the phase was ready to be sampled. Great care had to be exercised during sampling, in order not to disturb the equilibrium condition by changing the pressure of the mixture in the cell. Therefore while slowly removing the sample with the sampling pump, mercury was added at the same rate from the bottom of the cell with the displacement pump, thus keeping the pressure in the cell constant.
6. When enough sample had been taken, valve 19 was closed.
7. The vacuum was then cut off from the sampling container by closing 23. The sample was then expanded into the container by opening 20, and pushing the piston of the pump all the way up. Valve number 4 was then closed, and valves 11 and then 21 opened allowing helium to push mercury and any sample remaining in the lines into the container. Valve 22 was then closed. In the case of liquid samples, after taking the appropriate volume with the sampling pump, the double acting pump was used to provide mercury at the window level, and a few milliliters of mercury were then taken out of the cell at the sampling port.

As the samples were always diluted with helium gas before being injected into the chromatograph; a few trials

were made to determine a reasonable sample size and helium pressure, and it was found that good chromatographic responses were obtained when the high pressure vapor sample was about 1.4 ml and the liquid about 0.3 ml; while the helium pressure was about 30 psia.

To make sure that the liquid sample was vaporized before it was injected into the chromatograph, some calculations were carried out to decide the minimum temperature to be used. Appendix A describes the calculations. The sampling lines and container were wrapped with insulated heating tape, while the sampling pump bath was heated using an immersion heater; to make sure that the sample temperature is always higher than 100°F.

(b) Sampling Containers

A few attempts were made to develop the sampling method and decide upon the sampling container. The sampling container had to be of the proper size and shape to facilitate the transfer of the sample from the equilibrium cell to the chromatograph. Mention could briefly be made of some of the containers tried.

The first trial was done with a glass pear-shaped flask with replaceable silicon-sealed rubber at the top, two-way stopcock at the bottom and a three-way stopcock connected to the side of the flask. The sample was introduced into the flask from the side stopcock (number 22 in Figure 1), the helium from the bottom stopcock.

The sample was then taken by means of a syringe through the rubber stopper for subsequent analyses. The sample had to be injected directly into the column of the chromatograph by means of the syringe. An improvement of this arrangement was made by using another flask, having a neck at the top, with a replaceable silicon-sealed rubber stopper and a three-way stopcock at its side. Here the sample was introduced first, followed by helium through the side stopcock. This flask had the advantage over the previous one that the helium introduced through the side stopcock washed any remaining sample and mercury in the sampling pump and lines into the flask. The samples were taken for analyses the same way as before. However, the glass sphere connections and stopcocks of these flasks could not stand the helium pressure without leaking; and also during injection there was a possibility of hexane condensing in the syringe.

To overcome this difficulty, a steel bomb was used. Two stainless steel valves were connected to the bomb, one also connected to the sampling pump and the other to the vacuum line. After evacuating the bomb; the sample, mercury and helium were introduced into it. The bomb was then disconnected and well shaken for proper mixing. After proper mixing was achieved, the samples were taken for analyses through a hose connection which was attached to one of the valves. The injection of the samples was made into the loop of the chromatograph.

However, the possibility of hexane condensing in the injection lines was still present, and to avoid this a modification of the injection method was made, by connecting a hypodermic needle to one of the valves of the bomb allowing direct injection of the sample into the chromatographic column. This proved to be very efficient. The sampling container used during this work was a stainless steel bomb of 500 ml capacity, and having a diameter of about 2 1/4 inches. Two 1/4 inch Hoke stainless steel valves (number 23 and 22 in Figure 1) were connected to the end of the bomb.

(c) Injection Procedure

Great care was taken during the injection of the sample from the bomb into the chromatograph. The injection procedure can be summarized as follows:

1. The sample was flashed into the bomb from the sampling pump and the helium was admitted through valve number 11 in Figure 1 in order to push mercury and any sample out of the lines as mentioned above.
2. The bomb was disconnected from the sampling arrangement and the wrapped heating tape was then removed.
3. A vacuum was applied at the connection near valve 22 to free the autoclave coupling of any droplet of mercury that might have been left after sampling.
4. The bomb was then shaken, and good mixing of the contents of the bomb was assured due to the presence of mercury.

5. A hose connection, to which was soldered a fine hypodermic needle, was connected to valve 23.
6. The bomb was then placed in a heating oven maintained at a temperature of about 170°F.
7. A few minutes later, the bomb was removed from the oven, valve 23 was opened, and the sample allowed to purge into the atmosphere for about one minute, this insured that no air would be left in the valve and hypodermic needle, At the same time, hot air was blown over valve number 23 and the injection needle, to prevent any condensation of hexane due to the throttling effect.
8. A sample was then allowed into the chromatographic column 1 as shown in Figure 2 through a silicon seal. It was found that an injection time of about 2 to 3 seconds was enough to obtain a reasonable size of sample.
9. After injection, valve 23 was closed, the bomb shaken and then placed into the oven for the next injection.

The time that passed during injection while the sampling bomb was outside the oven was never enough to cool the contents of the bomb; the heat capacity of the stainless steel bomb being relatively so much higher than the contents. After the analysis was complete, the bomb was removed from the oven, its valves were opened and the mercury drained. The bomb was then connected to the sampling system, and helium allowed to flow through valve 11 Figure 1

for about 5 minutes to insure complete purging of the bomb and the system. The helium flow was then cut off and vacuum applied. When the bomb and pump were thoroughly evacuated, the system was ready for sampling.

Analytical Techniques

(a) Analytical Instrument

A Kromo-tog Model K-2 chromatograph manufactured by Burrell was used for analyzing the ternary mixtures. Two U shaped glass columns could be in a constant temperature air bath, its own temperature adjusting device, and its own constant temperature gas measuring and injecting systems.

The signal generated by the thermal conductivity detectors was recorded on a Moseley 7100B strip chart recorder, equipped with a disc chart integrator Model 229 manufactured for Hewlett-Packard by Disc Instruments Incorporated.

A filter bed packed with molecular sieve having a mesh size of 45-60 was installed between the helium supply tank and the chromatograph. The filter guards against drifting base lines by removing the impurities from the carrier gas, improves chromatography, and lengthens the life of the detector. A small 4-way Hamilton valve was installed on the chromatograph, to back purge by reversing the flow through the columns and thus extending the life of the columns.

A switch was inserted, allowing one to reverse the polarity of the recorder; and thus making it possible to record any peak while the carrier gas was flowing in the reversed direction.

(b) Chromatographic Methods

Due to the wide difference in boiling points between nitrogen and n-hexane, it was impossible for one column to make separation of the three components studied. The columns needed had to give a good separation of the components in a short time. A few columns were tried and some are mentioned below.

Starting with two one meter columns, they were packed and conditioned. The first column was packed with 25% silicon 550 on Celite, and the second with molecular sieve. The first column separated nitrogen and methane as one component and hexane as the other. The second column gave good separation for nitrogen and methane. The idea was to connect both columns in series, so that after getting the peaks of nitrogen and methane, the flow of helium and the polarity of the recorder were reversed so as to get a peak for hexane that was retained in the molecular sieve column. However it was found that a simpler way to apply this idea, was by packing the top 80 cms of a 2.5 meters column with 25% Si 550 on Celite and the rest with molecular sieve. Applying the same principle as above, a very good separation was obtained, but it was not possible to remove the

tailing obtained after reversing the flow. The peak corresponding to hexane was considered too wide and the length of the Si 550 portion insufficient, resulting in the tailing observed.

Since a standard 2.5 meter glass column was used in the chromatograph, it became necessary to find a material which when packed in a reasonable short length would be capable of separating methane and nitrogen, and therefore giving enough length for Si 550 to separate hexane. Activated charcoal was found adequate for this operation and the next trial was made with a column packed with Si 550 on Celite for the first 220 cms portion and about 30 cms of activated charcoal. This column gave a good separation of the components, but after about two months, it was found that the response of the chromatograph had changed and no longer gave reproducible results on consecutive days. As some deactivation of the charcoal seemed to have occurred, it was found preferable to change the column.

The next trial was to investigate the use of two separate columns, as if they were in two different chromatographs, and then to quantitatively relate the chromatograms which were obtained from both columns. Making two injections for every analysis; injecting a sample into the one meter column packed with Si 550 on Celite gave one peak for both methane and nitrogen and another peak for hexane. Then on injecting another sample into the other column which was packed with Si 550 on Celite for a length

of about 80 cms and molecular sieve for a length of about 170 cms nitrogen was separated from methane and a separate peak was obtained for each of them. Meanwhile, the hexane was still retained in the column and was eluted by reversing the flow. The problem was to find a common basis to relate the peaks obtained from both columns. A reasonable method was to inject a known volume of sample to each column and therefore relate the obtained results from both columns of the chromatograph. It was tried to fill up the loops connected to both columns of the chromatograph with the vapor to be analyzed at atmospheric pressure. The relative volume of the loops would give the factor needed to correlate the responses obtained from both columns. Using this method for a binary mixture composed of methane and hexane at two different equilibrium conditions (100°F and 1,000 psia, and 100°F and 500 psia) the results obtained did not coincide with those reported in the literature. The relative volumes of the loops were found not to be always the same. This fact along with the extreme precision required for analysis made the use of this method impracticable.

The next method tried was by connecting two columns in series and getting the complete analysis by one injection in less than 7 minutes. The chromatographic arrangement is shown in Figure 2. Column 1 is the one meter column, packed with 25% Silicon 550 on Celite, while column 2 has a length of 2.5 meters, about the first 80 cms of the

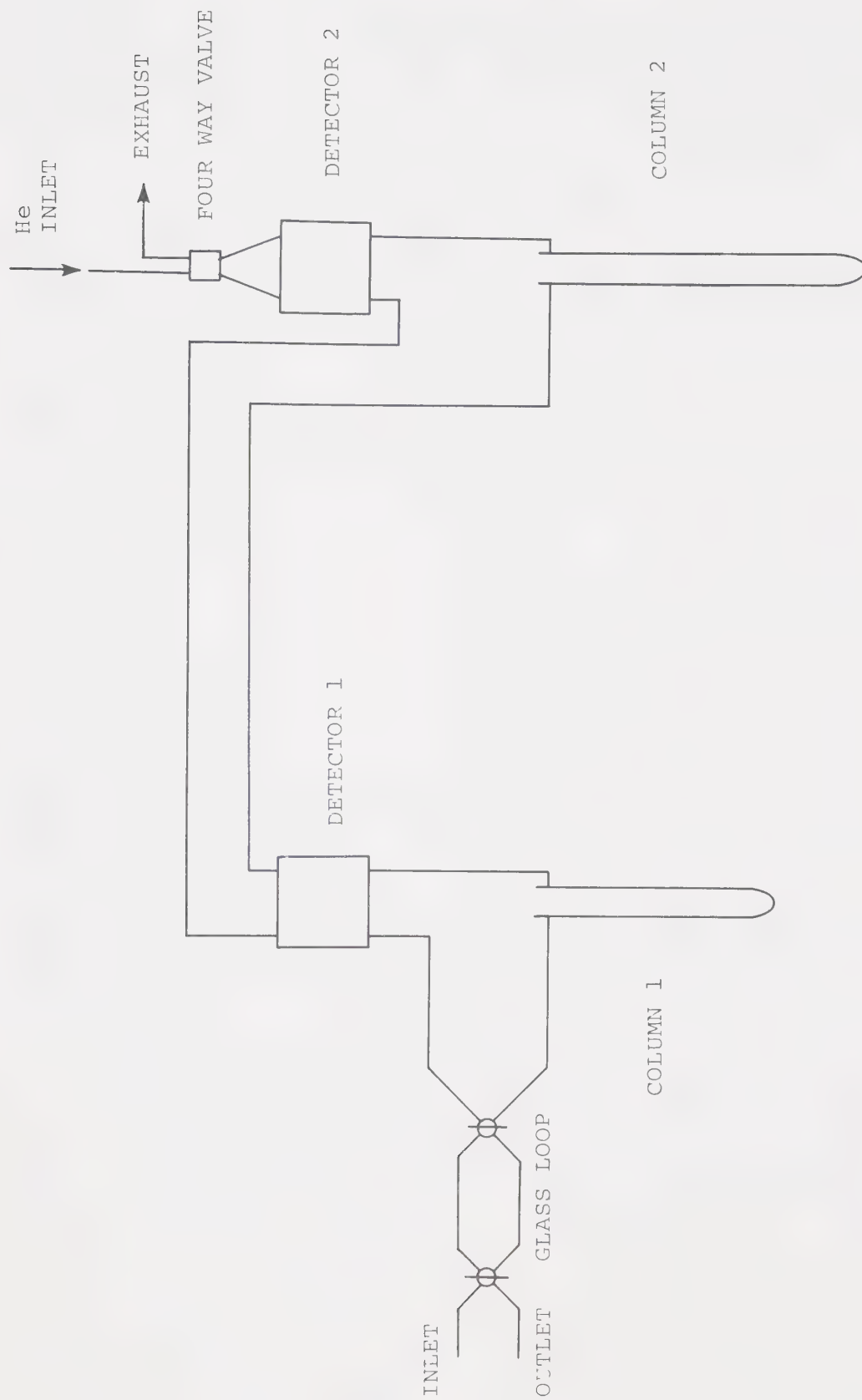


FIG. - 2 - CHROMATOGRAPHIC ARRANGEMENT

left leg are packed with 25% Si 550 on Celite and the rest with molecular sieve. The working side of detector 1 was placed between the two columns. A very good separation was obtained by this arrangement.

The column conditions were

Column 1	25% Si 550 on Celite
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Column length	1 meter
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Detector Current	200 mA
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Detector Bath Temperature	100°C
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Column Temperature	60°C
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Column 2	25% Si 550 on Celite, and Molecular Sieve
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Column Length	2.5 Meters
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Detector Current	200 mA
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Detector Bath Temperature	50°C
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Column Temperature	30°C
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Helium, the carrier gas, had a flow of about 32.7 ml/min., measured at the sample exhaust side of detector 2.

(c) Analytical Procedure

For the analysis of a ternary nitrogen-methane-n-hexane mixture, the procedure used was the following:

1. The one meter column was calibrated for pure n-hexane, and the 1.5 meters column for pure nitrogen and methane.
2. The sample of the ternary mixture was injected directly into the first column, giving a peak for both methane and nitrogen, and a peak for hexane. Thus the hexane

content of the sample could be obtained from its calibration.

3. As it came out of the first column, the sample was passed through the second column where hexane was retained by the molecular sieve and two peaks could be obtained for nitrogen and methane. From these peaks one may obtain the amounts of nitrogen and methane in the original sample.
4. The hexane retained by the second column was then washed out by backflushing.

A Hamilton one microliter syringe was used to inject different known amounts of n-hexane into the one meter column and get the calibration.

Known gas mixtures of Helium-Methane and Helium-Nitrogen having a Helium concentration of above 80%, were used to calibrate the columns for methane and nitrogen. A weighing technique was satisfactorily used to make the mixtures. Different amounts of methane and nitrogen were injected, using the glass loops of the chromatograph. The responses obtained from both columns were then recorded.

The calibration of the columns is given in Appendix B.

V RESULTS

The vapor liquid equilibrium behavior of the ternary nitrogen-methane-n-hexane system was studied at 40°F and 100°F. The experimental work was done at pressure of 500, 1,000 and 2,000 psia for both temperatures. The analyses of the equilibrium phases are shown in Table 1.

These data are shown graphically in the phase diagrams figures 3 through 9.

To smooth the experimental results, the data were plotted on a Y-X graph for each temperature studied. The best curve was drawn through the points for each component and the data were smoothed while keeping the relations $\Sigma Y = \Sigma X = 1.0$ satisfied.

The nitrogen concentration in the vapor phase was arbitrarily chosen to compare the results. Table 2 shows the equilibrium compositions and K-factors obtained from the smoothed curves at different concentrations of nitrogen in the vapor.

TABLE 1

Experimental Data

Temp. °F	Press. PSIA	Compositions, Mole Fraction					
		Vapor Phase			Liquid Phase		
		N ₂	C ₁	n-C ₆	N ₂	C ₁	n-C ₆
40	500	.14	.853	.007	.009	.187	.804
		.729	.265	.006	.038	.059	.903
		-	.993	.007	-	.223	.777
		.995	-	.005	.042	-	.958
	1000	.155	.839	.006	.015	.282	.703
		.75	.237	.013	.062	.099	.839
		-	.994	.006	-	.355	.645
		.996	-	.004	.084	-	.916
	2000	.168	.817	.015	.04	.463	.497
		.764	.229	.007	.136	.158	.706
		-	.978	.022	-	.577	.423
		.996	-	.004	.172	-	.828
100	500	.016	.955	.028	.002	.175	.823
		.054	.915	.031	.006	.168	.826
		.145	.822	.033	.01	.143	.847
		.673	.29	.037	.04	.062	.898
	1000	.962	-	.038	.054	-	.946
		.696	.274	.03	.07	.099	.831
		.059	.916	.025	.006	.276	.718
		.984	-	.016	.099	-	.901
	2000	.335	.634	.031	.071	.339	.591
		.017	.946	.037	.007	.495	.498
		.976	-	.024	.188	-	.812

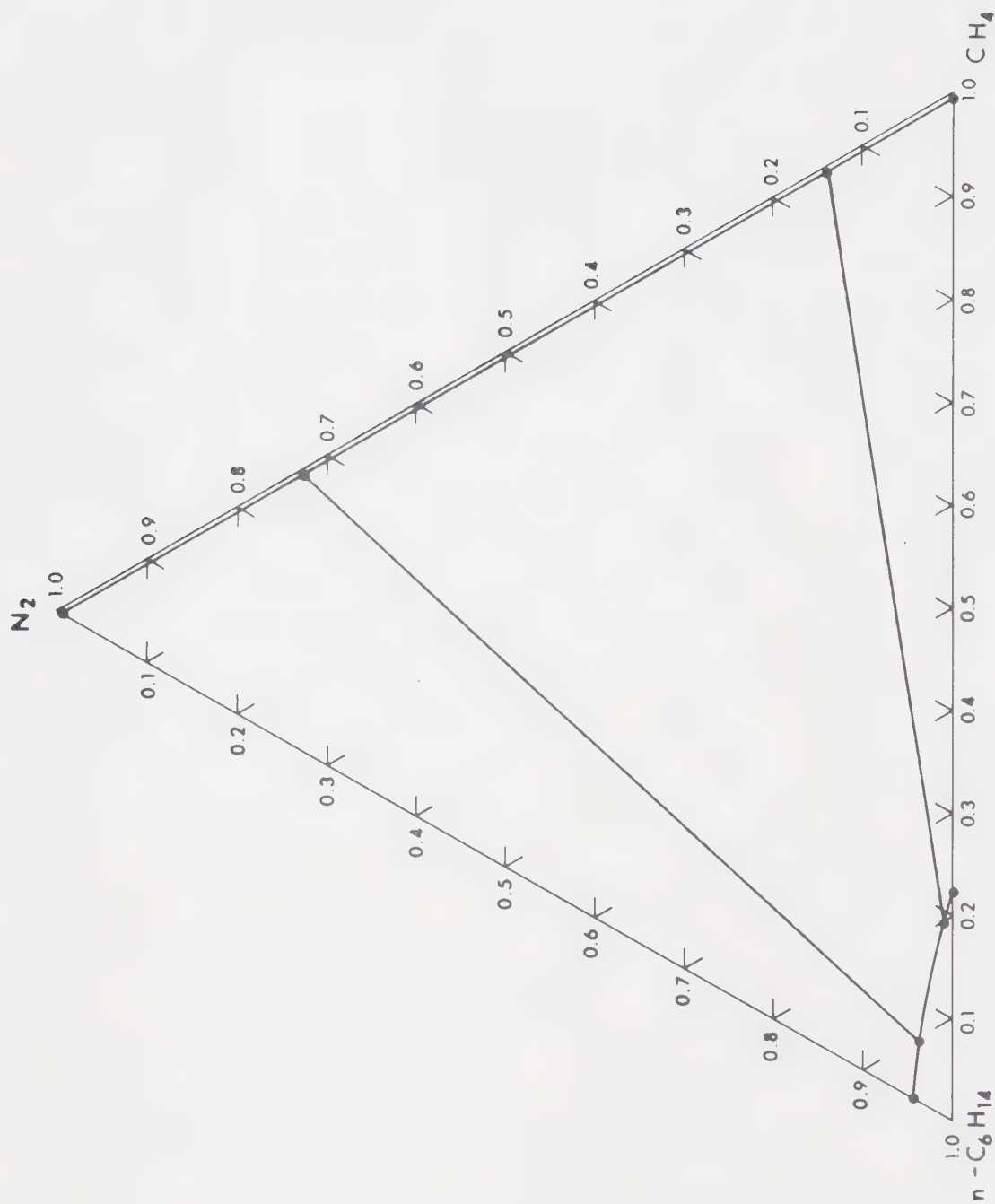


FIG.-3 - PHASE COMPOSITIONS IN THE TERNARY SYSTEM AT : 500 psia. AND 40°F.

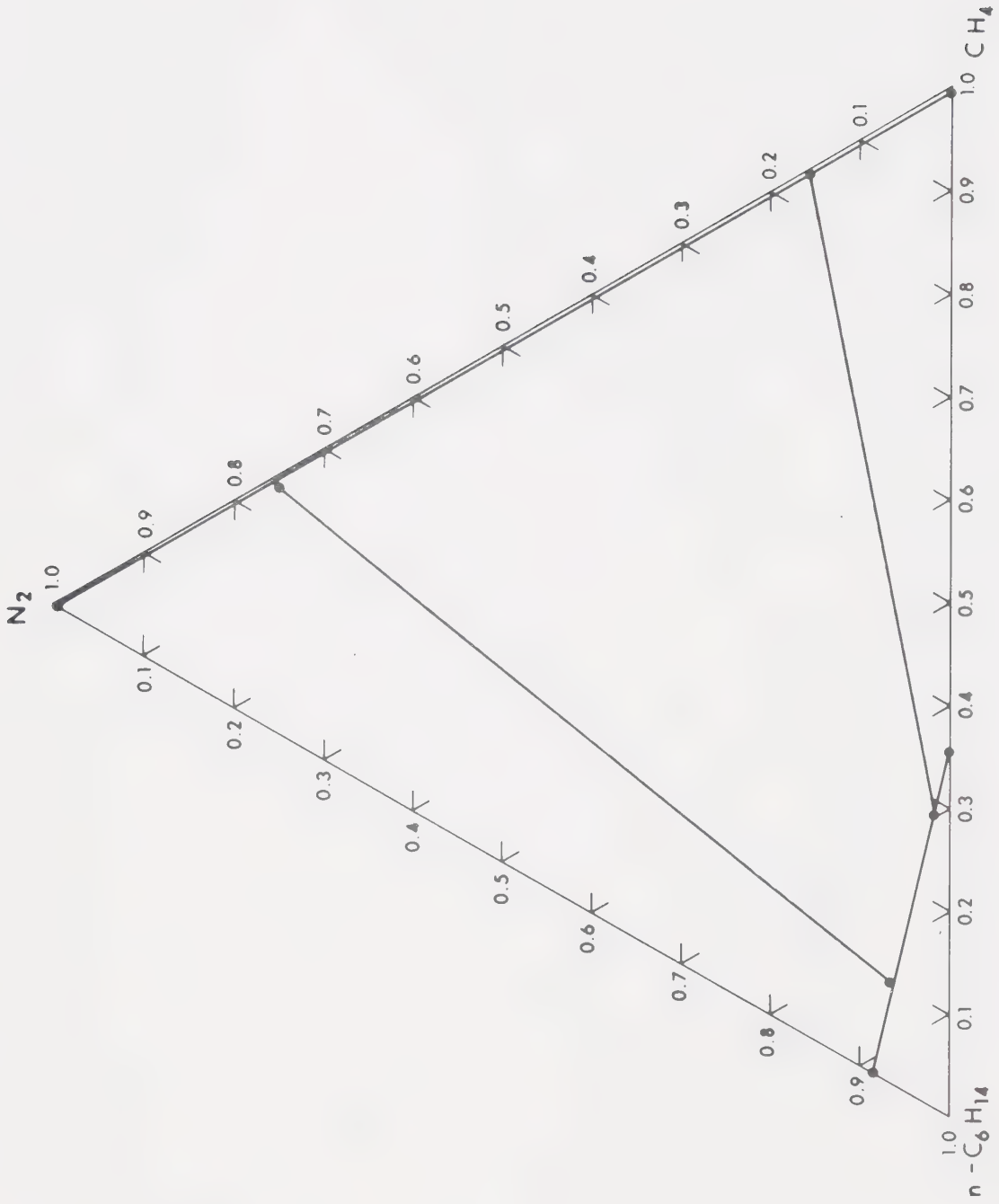


FIG.-4 - PHASE COMPOSITIONS IN THE TERNARY SYSTEM AT 1000 psia. AND 40°F.

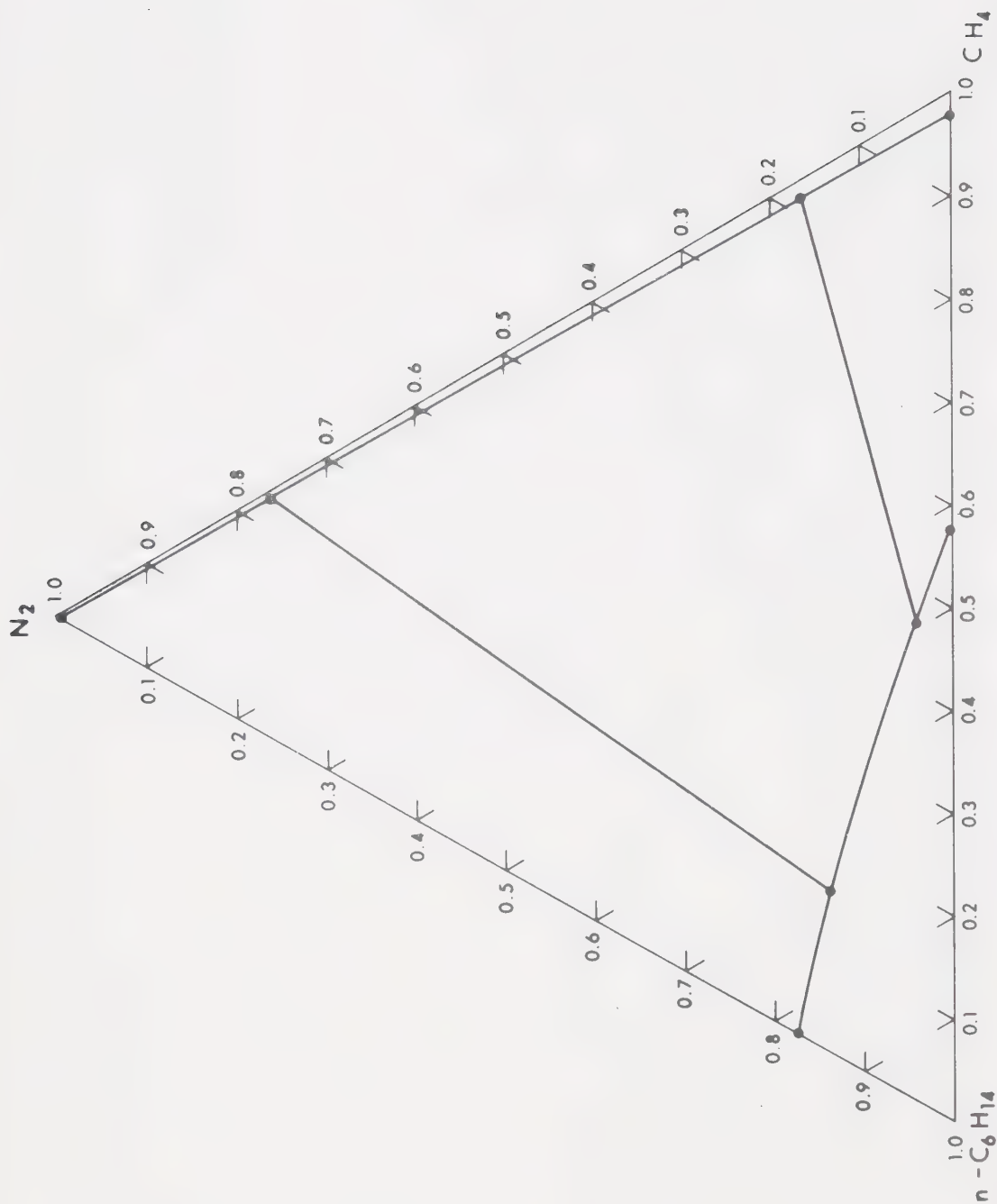


FIG.-5 - PHASE COMPOSITIONS IN THE TERNARY
SYSTEM AT 2,000 psia AND 40°F

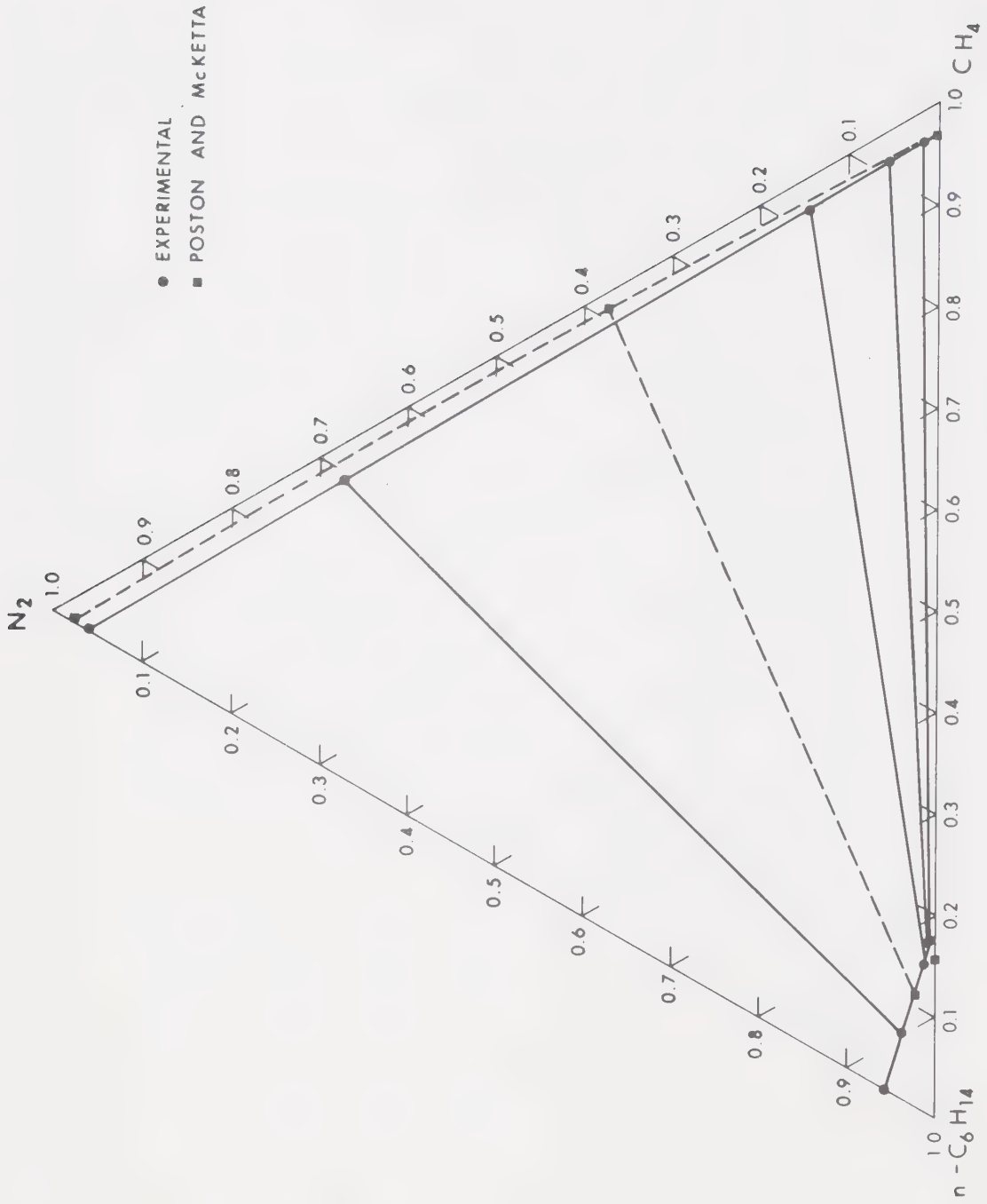


FIG.-6- PHASE COMPOSITIONS IN THE TERNARY SYSTEM AT 500 psia. AND 100 °F

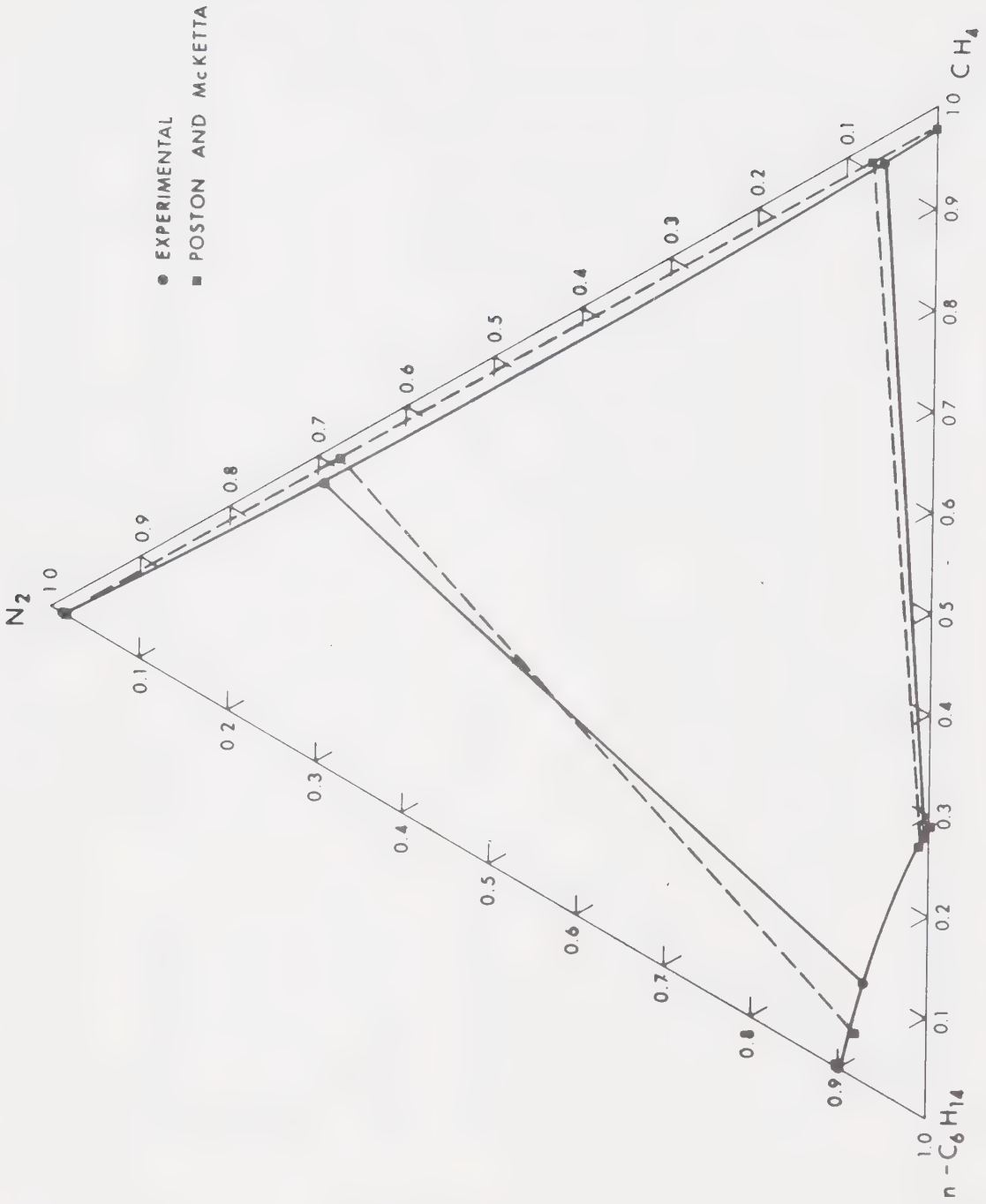


FIG.-7- PHASE COMPOSITIONS IN THE TERNARY SYSTEM AT 1,000 psia AND 100°F

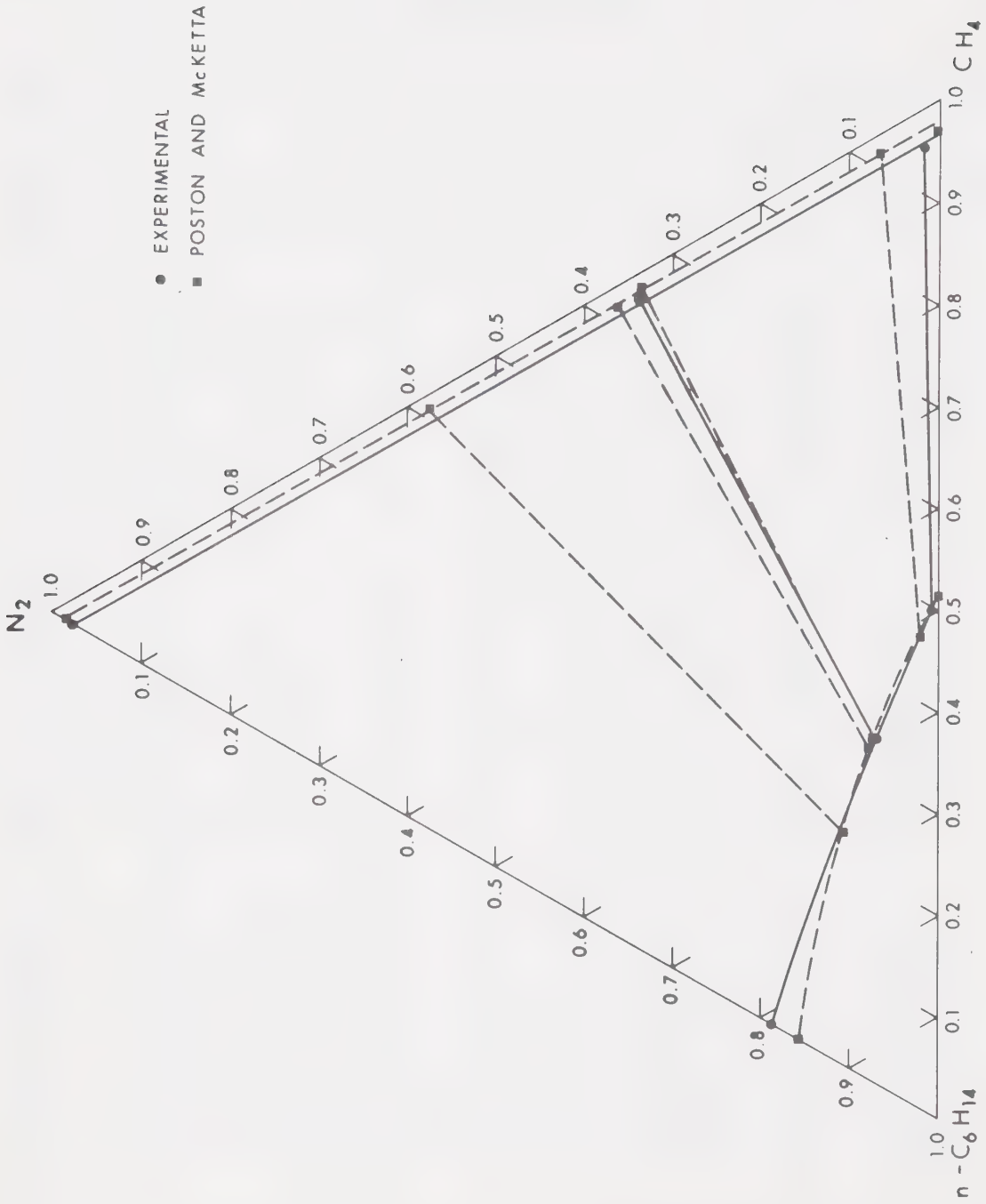


FIG.-8 - PHASE COMPOSITIONS IN THE TERNARY SYSTEM AT 2,000 psia, AND 100°F.

TABLE 2

Smoothed Ternary Data

Nitrogen			Methane			n-Hexane		
Y	X	K	Y	X	K	Y	X	K
40°F, 500 PSIA								
.100	.006	16.7	.896	.2	4.48	.004	.794	.0050
.200	.013	16.0	.796	.177	4.50	.004	.811	.0049
.300	.019	16.2	.696	.155	4.49	.004	.827	.0048
.400	.024	16.7	.595	.132	4.51	.005	.844	.0059
.500	.029	17.2	.495	.110	4.5	.005	.861	.0058
.600	.033	18.2	.395	.088	4.50	.005	.879	.0057
.700	.037	18.9	.295	.066	4.47	.005	.897	.0056
.800	.039	20.3	.195	.043	4.54	.005	.918	.0054
40°F, 1000 PSIA								
.1	.009	11.1	.895	.312	2.87	.005	.679	.0074
.2	.018	11.1	.796	.277	2.87	.004	.705	.0057
.3	.025	11.5	.696	.244	2.85	.004	.730	.0055
.4	.035	11.4	.595	.212	2.81	.005	.753	.0066
.5	.043	11.6	.495	.182	2.72	.005	.775	.0065
.6	.051	11.8	.395	.150	2.63	.006	.799	.0075
.7	.059	11.9	.294	.117	2.51	.006	.824	.0073
.8	.067	11.9	.194	.082	2.37	.006	.851	.0071
40°F, 2000 PSIA								
.1	.025	4.0	.88	.506	1.74	.02	.469	.0426
.2	.046	4.35	.783	.448	1.75	0.17	.506	.0336
.3	.065	4.62	.686	.395	1.74	.014	.540	.0259
.4	.082	4.88	.588	.347	1.70	.012	.571	.0210
.5	.098	5.10	.489	.297	1.65	.011	.605	.0182
.6	.112	5.36	.39	.247	1.58	.010	.641	.0156
.7	.127	5.51	.292	.195	1.50	.008	.678	.0118
.8	.142	5.62	.195	.138	1.41	.005	.720	.0069

TABLE 2 (Continued)

Nitrogen			Methane			n-Hexane		
Y	X	K	Y	X	K	Y	X	K
			100°F, 500 PSIA					
.1	.008	12.2	.868	.159	5.46	.032	.833	.038
.2	.015	13.3	.768	.143	5.37	.032	.842	.038
.3	.021	14.3	.668	.126	5.30	.032	.853	.038
.4	.027	15.0	.567	.108	5.25	.033	.865	.038
.5	.032	15.6	.466	.090	5.18	.034	.878	.039
.6	.037	16.2	.364	.072	5.06	.036	.891	.040
.7	.042	16.7	.264	.053	4.98	.036	.905	.040
.8	.047	17.1	.163	.034	4.79	.037	.919	.040
			100°F, 1000 PSIA					
.1	.011	9.09	.872	.265	3.29	.028	.724	.0387
.2	.021	9.52	.77	.239	3.22	.030	.740	.0405
.3	.03	10.0	.669	.212	3.16	.031	.758	.0409
.4	.042	9.52	.568	.185	3.07	.032	.773	.0414
.5	.052	9.62	.467	.157	2.97	.033	.791	.0417
.6	.062	9.68	.368	.129	2.85	.032	.809	.0396
.7	.071	9.86	.270	.099	2.73	.030	.830	.0361
.8	.081	9.88	.172	.068	2.53	.028	.851	.0329
			100°F, 2000 PSIA					
.1	.024	4.17	.868	.461	1.88	.032	.515	.062
.2	.046	4.35	.769	.408	1.88	.031	.546	.057
.3	.067	4.48	.67	.356	1.88	.03	.577	.052
.4	.087	4.60	.57	.303	1.88	.03	.61	.049
.5	.106	4.72	.47	.25	1.88	.03	.644	.047
.6	.124	4.84	.371	.197	1.88	.029	.679	.043
.7	.142	4.93	.272	.145	1.88	.028	.713	.039
.8	.159	5.03	.173	.092	1.88	.027	.749	.036

VI DISCUSSION

Most of the available correlations used to predict the equilibrium relations for hydrocarbon systems exclude nitrogen. However, the equilibrium ratios could be calculated for systems composed of nitrogen and hydrocarbons by the Hadden, Grayson and Winn Nomograph (21, 78) and by the NGPSA Engineering Data Book (37), and by the Chueh-Prausnitz method (45).

Comparison of K-factors with Winn and NGPSA Methods

To calculate the K-factors by the Winn Nomograph and the NGPSA, the critical locus of the nitrogen-n-hexane system was needed in order to estimate the convergence pressure of the ternary mixture.

Critical Loci

To calculate the critical loci of the nitrogen-n-hexane and methane-n-hexane systems, the method presented by Chueh (12) was used.

The critical temperatures and the critical volumes of binary mixtures were given by

$$T_{CT} = \theta_1 T_{C_1} + \theta_2 T_{C_2} + 2 \theta_1 \theta_2 \tau_{12} \quad (26)$$

$$\text{and } v_{CT} = \theta_1 v_{C_1} + \theta_2 v_{C_2} + 2 \theta_1 \theta_2 v_{12} \quad (27)$$

where θ is the surface fraction, and is defined by

$$\theta_i = \frac{x_i v_{C_i}^{2/3}}{x_1 v_{C_1}^{2/3} + x_2 v_{C_2}^{2/3}} \quad (28)$$

where τ_{12} and v_{12} are correlating parameters characteristic of the binary mixture.

The critical pressure was calculated using the Redlich-Kwong equation of state with some alterations. The calculated critical temperature and volume were used in the equation, together with K_{12} which is a constant characteristic of the component 1-component 2 interaction.

Three constants are thus needed to calculate the critical locus of a binary mixture. Table 3 shows the constants used.

TABLE 3

Binary Mixture	$\frac{v_{12}^2}{v_{C_1} + v_{C_2}}$	$\frac{\tau_{12}^2}{T_{C_1} + T_{C_2}}$	K_{12}
Nitrogen-Hexane	-1.012	0.54	0.18
Methane-Hexane	-0.87	0.25	0.08

Poston and McKetta (42) gave the composition and the critical pressure of a nitrogen-n-hexane mixture at

280°F. This experimental point was fitted and the constants shown in Table 3 were obtained. The constant used to calculate the critical temperature of the mixture was determined first from a knowledge of the critical temperature and composition of the experimental point. K_{12} was obtained by graphically extrapolating values obtained for other systems containing paraffin hydrocarbons and nitrogen. The parameter used to calculate the critical volume was then determined by means of the two other constants and the experimental point.

For the methane-n-hexane system the first two constants were obtained from curves available for paraffin-paraffin systems in terms of pure component critical constants, while K_{12} was given by Chueh (12).

Tables 4 and 5 give the results obtained, and Figure 9 shows the predicted loci, together with the experimental points given by Poston. The composition of the critical points for the methane-n-hexane system was not experimentally available.

From a knowledge of the critical locus of the nitrogen-n-hexane system, the convergence pressures of this binary were obtained at the experimental temperatures. Equation (17) was then applied to calculate the convergence pressure of the ternary system. The critical temperature of methane was used in this equation because the experimental temperatures were higher than the critical

TABLE 4

Critical Locus of the Nitrogen-n-hexane System

Composition Nitrogen Mole Fraction	P _{CM} calc. PSJA	P _{CM} exp. PSIA	T _{CM} calc. °F	T _{CM} exp. °F	V _{CM} calc. cu ft./lb mole
1.0	492.0		-233.1		1.44
.95	2749.8		-86.9		1.192
.90	5185.6		25.4		1.146
.85	6297.9		112.8		1.234
.80	5990.8		181.7		1.410
.75	5144.4		236.4		1.645
.70	4291.2	4293.0	280.2	280.0	1.916
.60	3010.8		343.8		2.516
.50	2192.7		385.6		3.14
.40	1638.7		413.2		3.753
.30	1234.2		431.3		4.339
.20	914.1		443.0		4.892
.10	660.4		450.2		5.408
0.0	439.0		454.2		5.890

TABLE 5

Critical Locus of the Methane-n-hexane System

Composition Methane Mole Fraction	P _{CM} calc. PSIA	T _{CM} calc. °F	V _{CM} calc. cu ft/lb mole
1.0	673.0	-116.1	1.59
.95	1617.9	-21.02	1.424
.90	2535.6	55.93	1.413
.85	3015.3	118.95	1.508
.80	3033.2	171.11	1.675
.75	2804.6	214.66	1.892
.70	2503.0	251.33	2.141
.60	1945.9	299.01	2.692
.50	1523.8	351.54	3.270
.40	1207.1	383.57	3.844
.30	960.0	408.11	4.399
.20	758.6	427.20	4.926
.10	588.1	442.24	5.423
0.0	439.0	454.2	

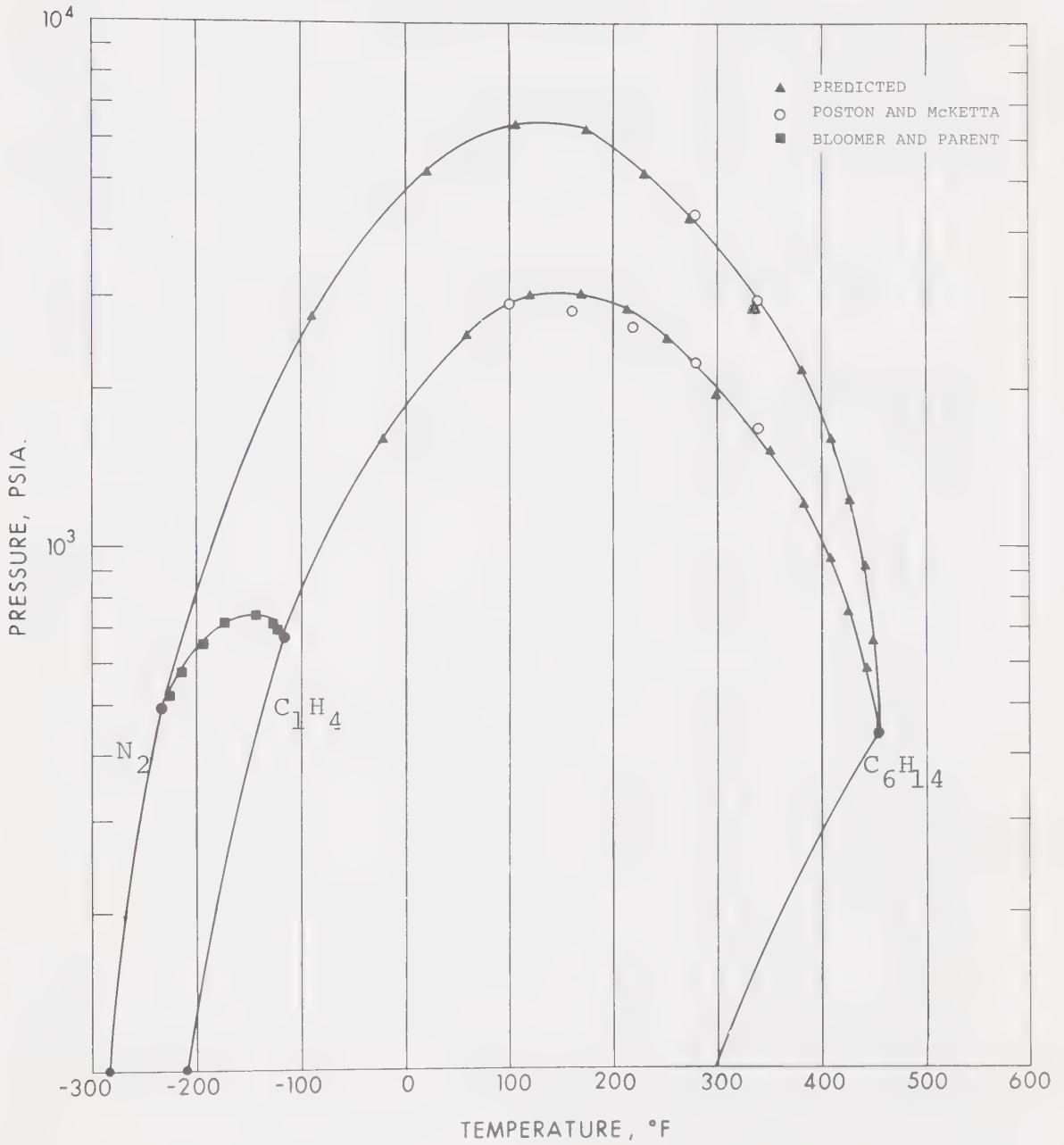


FIG.-9- CRITICAL LOCI

temperature of methane.

$$P_K = \frac{m_2 P_2 + m_3 P_3}{m_2 + m_3} \quad (17)$$

The liquid phase composition obtained from the smoothed experimental data were used to calculate the convergence pressure of the ternary system.

The K-factors were then read using the Winn Nomograph given by Hadden and Grayson.

The equilibrium ratios for nitrogen, methane and n-hexane were also obtained at the experimental conditions by making some interpolation of values given in the NGPSA Engineering Data Book. The K-factors for each component were read from the book at the experimental conditions at convergence pressures of 2,000, 4,000 and 10,000 psia. Graphs were then constructed, where the K-factors were plotted against the convergence pressure using the pressure as a parameter at different experimental temperatures. From these graphs the equilibrium ratios were obtained at the convergence pressures of the experiments. The experimental K-factors of the nitrogen-methane-n-hexane system are compared in Table 6 to the K-factors obtained from the Winn Nomograph and those from the NGPSA Engineering Data Book.

It could be said that the predictions made by the Winn Nomograph are better than those from the NGPSA. However, both methods cannot be accepted as giving good

predictions of the K-factors in this case. The reason could be that equation (17) should not be applied for this system, because the mass fraction of hexane was always high in the liquid phase, which made the change in the convergence pressure calculated by equation (17) quite small. Therefore, the effect of the change in the total composition was not well represented by the convergence pressure. It could then be concluded that this equation could not be applied to calculate the convergence pressure in this case, and that more data are needed to obtain a better estimate of the convergence pressure.

TABLE 6

Comparison of K-factors by Winn Nomograph and NGPSA
K-factors with experimental K-factors

Temp. OF	Pres- sure PSIA	Average Percent Deviation					
		Winn Nomograph			NGPSA		
		N ₂	CH ₄	n-C ₆ H ₁₄	N ₂	CH ₄	n-C ₆ H ₁₄
40	500	4.5	15.1	61.9	1.3	14.9	63.5
	1000	20.3	8.1	35.8	27.3	14.0	73.4
	2000	2.5	7.5	31.8	13.3	21.9	45.5
100	500	25.8	29.5	46.2	57.6	28.0	31.3
	1000	4.7	18.1	41.0	22.3	25.5	17.9
	2000	14.9	3.7	3.1	20.3	17.6	27.1

Equilibrium Composition by the Chueh-Prausnitz Method

To predict the bubble point temperature and the vapor composition of the nitrogen-methane-n-hexane system in the temperature range from 500°R to 800°R, a knowledge of the liquid composition and the pressure are needed. Prausnitz and Chueh (45) describe the method in detail. The critical properties and other constants characteristic of the pure components are required. For the possible binaries, these properties and constants are needed, together with the self interaction constants and the Henry's constants both given as functions of temperature.

The binary parameters needed were either available or were determined during the calculations previously made to predict the critical loci. The self-interaction constant was not available for the binary nitrogen-n-hexane system. All the other relations were given by Prausnitz and Chueh for a smaller range of temperature than the one of this work. They were extended to cover the experimental temperature range by the methods explained in the text.

The HENRY'S program and the FITTING program given by Prausnitz and Chueh were used to determine the self-interaction constant for the nitrogen-n-hexane binary system as a function of temperature. The experimental data of Poston and McKetta (42) together with

those obtained in this work were used in making the calculations. Table 7 shows the results obtained. As shown in the table, the results predicted are not very accurate. This cannot lead to the conclusion that this method should not be applied to predict the ternary equilibrium compositions, because some errors could have been introduced during the extrapolation of the Henry's and the self-interaction constants. Also, the binary experimental data used to calculate the self-interaction constant for the nitrogen-n-hexane system were not complete enough to give a truly representative value.

However, from Figure 9 it may be concluded that the Chueh-Prausnitz method gives a good prediction of the critical locus for the binary systems containing methane and hexane.

Appendix C contains a comparison of the temperature and the vapor composition of the nitrogen-methane-n-hexane system calculated by the Chueh-Prausnitz method with the experimental data given by Boomer and Johnson (8) and Poston and McKetta (43). A comparison of the results by Poston and McKetta for the nitrogen-n-hexane and methane-n-hexane systems are also included.

It should be mentioned that while calculating the self-interaction constants α for the nitrogen-n-hexane system by the FITTING program, the corresponding dilation constants n were given in the output of the program.

Temperature and Vapor Composition Calculated by Chueh-Prausnitz Method

E X P E R I M E N T A L					P R E D I C T E D			
P (PSIA)	T (°R)	X, Mole Fraction		Y, Mole Fraction		T (°R)	Y, Mole Fraction	
		n-C ₆	C ₁ N ₂	n-C ₆	C ₁ N ₂		n-C ₆	C ₁ N ₂
500	500	.834	.187 .009	.007	.853 .14	495	.005	.890 .105
500	500	.903	.059 .038	.006	.265 .729	559	.018	.368 .614
1000	500	.703	.282 .015	.006	.839 .155	542	.013	.881 .106
1000	500	.839	.099 .062	.013	.237 .75	754	.203	.380 .417
2000	500	.706	.158 .136	.007	.229 .764	798	.436	.277 .287
2000	500	.497	.463 .040	.015	.817 .168	557	.029	.839 .132
500	560	.847	.143 .010	.033	.822 .145	543	.013	.838 .149
500	560	.898	.062 .040	.037	.29 .673	543	.013	.368 .619
500	560	.823	.175 .002	.029	.955 .016	527	.010	.963 .028
500	560	.826	.168 .006	.031	.915 .054	523	.009	.910 .082
1000	560	.831	.099 .070	.030	.274 .696	600	.030	.364 .606
1000	560	.718	.276 .006	.025	.916 .059	574	.022	.932 .046
2000	560	.591	.339 .071	.031	.634 .335	603	.045	.683 .272
2000	560	.498	.495 .007	.037	.946 .017	596	.048	.929 .023

Some values of η and the values of α calculated from them were neglected before plotting and fitting this constant. The reason is that the model presented by Prausnitz and Chueh does not allow for negative η .

The FITTING program gives intermediate values from which α could be calculated once η is known. This procedure gave values for α that were far from those listed for similar systems and therefore these results were not used.

NOMENCLATURE

f	fugacity
f^0	reference fugacity
f''	denotes a function of variables
K	equilibrium ratio
K_{12}	characteristic constant for 1-2 interaction
M	compositon parameter based on mass fraction
m	mass fraction
P	total pressure of system
p	partial pressure of a component
p^0	vapor pressure of a component
P_C	critical pressure
P_{CM}	critical pressure of a mixture
P_K	convergence pressure
R	gas constant
T	temperature of system
T_C	critical temperature of a component
T_{CM}, T_{CT}	critical temperature of a mixture
v	molar volume of the vapor or liquid phase
v_C	critical volume
v_{CM}, v_{CT}	critical volume of a mixture
x	mole fraction in liquid phase
y	mole fraction in vapor phase
z	compressibility factor

Greek letters

α	interaction constant
η	dilation constant
θ	surface fraction
v_{12}	correlating parameter for critical volume
τ_{12}	correlating parameter for critical temperature
γ	activity coefficient
δ	solubility parameter
v	fugacity coefficient of pure liquid component
ϕ	fugacity coefficient of component in vapor mixture
ω	acentric factor

Superscript

L	liquid phase
V	vapor phase
(P^r)	at constant reference pressure
o	reference state

Subscripts

C	critical
i	component i
M	mixture
-	a bar at the top denotes the value of a property in a mixture

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A P P E N D I C E S

Appendix A

To make sure that n-hexane in the liquid samples would be transferred to the sampling bomb in the gaseous state, and no condensation would take place, the following calculation was made:

$$p V = NZRT$$

where V = Volume of the sampling container, taken as 500 ml

R = Gas constant, taken as 670 ml.psia/gm mole $^{\circ}\text{R}$

T = Temperature of the sampling container, $^{\circ}\text{R}$

p = Partial pressure of n-hexane, calculated in psia
at Temperature T, assuming ideal gas behavior

Z = Compressibility factor, taken as 1.0 at the
pressure and temperature in the sampling con-
tainer

N = Moles of n-hexane sampled

Specific gravity of n-hexane = 0.66

Molecular weight of n-hexane = 86.2

Assuming the volume of n-hexane taken from the equilibrium
cell = 0.4 ml.

$$\begin{aligned} p &= \frac{NZRT}{V} \\ &= \frac{(0.4)(0.66)}{86.2} (1.0) \frac{670}{500} T \end{aligned}$$

By calculating the partial pressure at different temperatures and from a knowledge of the vapor pressure of n-hexane, Table A1 and Figure A1 were constructed.

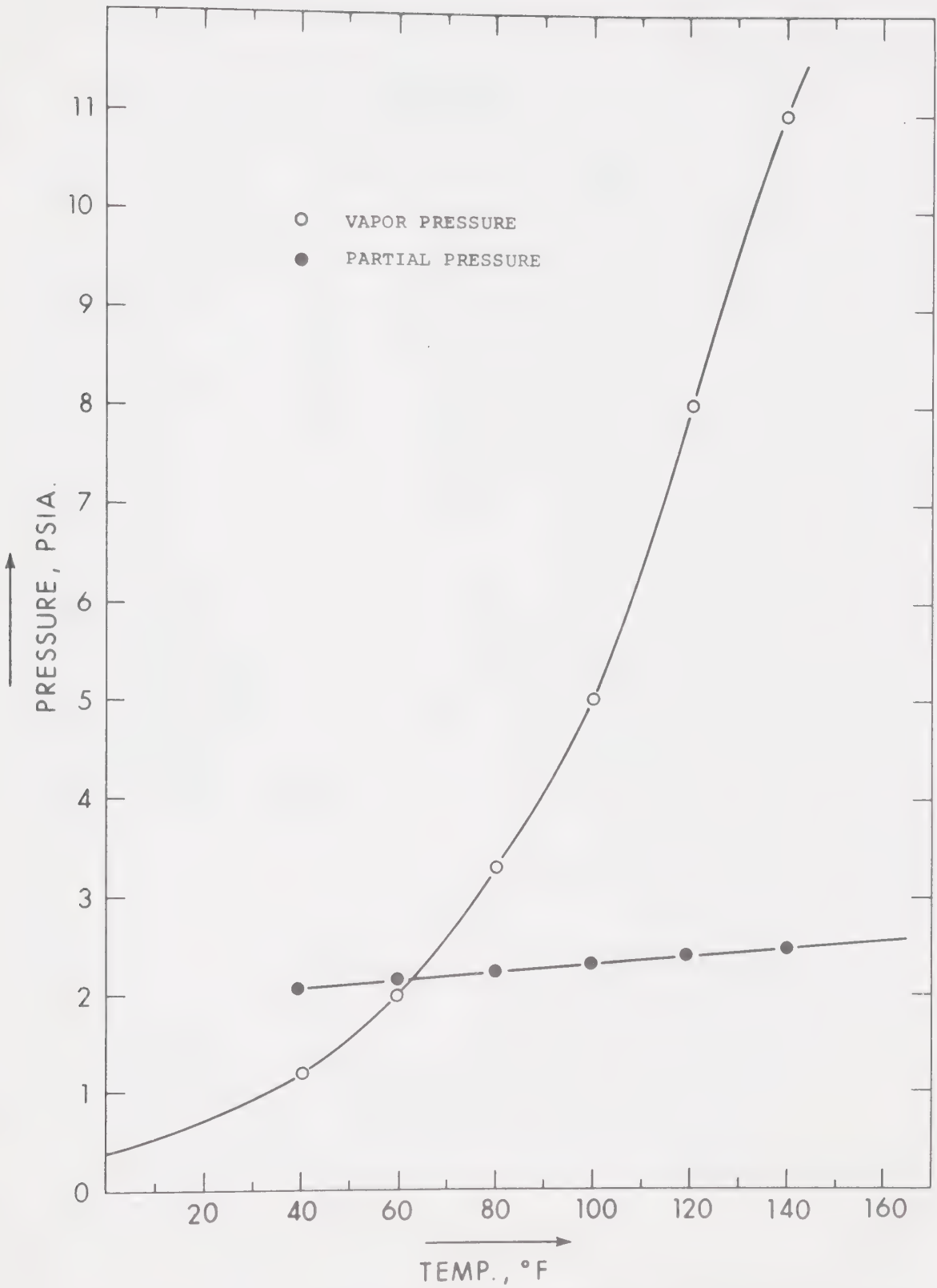


FIG. -A1- DETERMINATION OF THE MINIMUM ALLOWABLE TEMPERATURE OF THE SAMPLING SYSTEM.

TABLE A1

$t, ^\circ\text{F}$	p, psi	P°, psi
40	2.06	1.2
60	2.14	2.0
80	2.22	3.3
100	2.30	5.0
120	2.39	8.0
140	2.47	11.0

P° is the vapor pressure of normal hexane.

Therefore if t , the sample temperature is always maintained higher than 100°F , liquid hexane will definitely be in the vapor state.

Appendix B

Calibration of the Chromatographic Columns

Column 1 was calibrated for n-hexane, while column 2 was for nitrogen and methane. When the component to be analyzed was eluted from the column, it passed through the thermal conductivity detector and a peak was subsequently drawn by the recorder. The area under the peak was measured by the disk integrator. The number of moles of material entering the detector cell was proportional to the area under the peak. The relation between the number of moles of material that was added to each column and the area under the corresponding peak was represented by a straight line down to an experimentally obtained limit. From this limit to the origin, the function was represented by a quadratic equation which passed through the origin and intersected the linear relationship tangentially. Therefore, if Y = number of moles and X = area under the peak, the relation $Y = CX + DX^2$ will hold for X smaller than the experimentally obtained limit, above which the relation $Y = AX + B$ applies.

Where C , D , A and B are constants for the component to be analyzed.

The experimentally obtained calibration points were fitted using a least square method. The results are presented in Table B1.

TABLE B1
Calibration of the Chromatographic Columns

Column Number	Component	Attenuation	A x 10 ⁸	B x 10 ¹¹	Limit	C x 10 ⁸	D x 10 ¹⁴
1	n-Hexane	10	.132415	-5424.06	651.0	.115751	12.7985
		20	.258528	1372.0	193.95	.259943	-.364726
2	Nitrogen	10	.329809	-11882.9	792.5	.29982	18.9204
		20	.637951	-8824.32	502.0	.602794	35.017
	Methane	10	1.67874	-18788.0	273.5	1.54135	251.17
		20	1.54135	.25117	36.0	.898718	-3500.09

Appendix C

TABLE C1

Comparison of the Temperature and Vapor Composition Calculated by Chueh-Prausnitz Method with the Experimental Values for the Nitrogen-n-Hexane Binary (42)

E X P E R I M E N T A L						P R E D I C T E D		
P (PSIA)	T (°R)	X, Mole Fraction		Y, Mole Fraction		T (°R)	Y, Mole Fraction	
		n-C ₆	N ₂	n-C ₆	N ₂		n-C ₆	N ₂
250	560	.974	.026	.042	.958	635	.103	.897
500	560	.947	.053	.019	.981	644	.072	.928
1000	560	.899	.101	.017	.983	820	.404	.596
1500	560	.863	.137	.011	.989	819	.659	.341
2000	560	.845	.155	.015	.985	810	.619	.381
2500	560	.81	.190	.012	.988	794	.546	.454
3000	560	.782	.218	.014	.986	773	.479	.521
3500	560	.747	.253	.016	.984	755	.41	.59
4000	560	.71	.290	.017	.983	694	.26	.74
4500	560	.67	.330	.0125	.975	612	.096	.904
5000	560	.641	.359	.02	.980	570	.076	.924
250	620	.975	.025	.096	.904	662	.153	.847
500	620	.949	.051	.058	.942	726	.208	.792
1000	620	.901	.099	.036	.964	823	.427	.573
1500	620	.856	.144	.027	.973	816	.646	.354
2000	620	.818	.182	.027	.973	805	.578	.422
2500	620	.789	.211	.028	.972	792	.516	.484
3000	620	.756	.244	.036	.964	771	.444	.556
3500	620	.622	.278	.041	.959	716	.365	.635
4000	620	.689	.311	.042	.958	644	.119	.881
4500	620	.67	.330	.040	.960	612	.096	.904
5000	620	.609	.391	.042	.958	554	.059	.941
250	680	.977	.023	.211	.789	703	.265	.735
500	680	.953	.047	.131	.869	778	.360	.640
1000	680	.905	.095	.079	.921	830	.475	.525
1500	680	.85	.150	.072	.928	814	.630	.37
2000	680	.801	.199	.072	.928	600	.031	.969
2500	680	.758	.242	.073	.927	590	.032	.968
3000	680	.717	.283	.074	.926	581	.034	.966
3500	680	.665	.335	.089	.911	562	.033	.967
4000	680	.62	.380	.101	.899	556	.036	.964

TABLE C2

E X P E R I M E N T A L						P R E D I C T E D		
P (PSIA)	T (°R)	X, Mole Fraction		Y, Mole Fraction		T (°R)	Y, Mole Fraction	
		n-C ₆	C ₁	n-C ₆	C ₁		n-C ₆	C ₁
500	560	.847	.153	.031	.969	575	.025	.975
1000	560	.714	.286	.02	.980	581	.025	.975
1500	560	.596	.404	.021	.979	588	.033	.967
2000	560	.489	.511	.03	.970	597	.048	.952
2500	560	.362	.638	.031	.969	568	.051	.949
2700	560	.306	.694	.03	.970	551	.051	.949
2765	560	.285	.715	.032	.968	543	.05	.951
2845	560	.244	.756	.036	.964	526	.045	.955
2825	560	.26	.740	.038	.962	533	.047	.953
2870	560	.236	.764	.043	.957	523	.044	.956
500	620	.865	.135	.063	.937	629	.061	.939
1000	620	.742	.250	.047	.953	639	.057	.943
1500	620	.629	.371	.038	.962	656	.073	.927
2000	620	.515	.485	.054	.946	663	.092	.908
2500	620	.606	.594	.072	.928	488	.145	.855
2700	620	.332	.668	.087	.913	565	.055	.945
2750	620	.299	.701	.089	.911	549	.052	.948
2795	620	.297	.703	.115	.885	550	.053	.947
500	680	.881	.119	.129	.871	690	.140	.86
1000	680	.76	.240	.089	.911	695	.111	.889
1500	680	.649	.351	.092	.908	722	.147	.853
2000	680	.523	.477	.105	.895	812	.393	.607
2500	680	.396	.604	.139	.861	600	.067	.933
2540	680	.382	.618	.178	.822	589	.063	.937
2580	680	.35	.650	.183	.817	568	.055	.945
2615	680	.325	.675	.216	.784	556	.050	.950
500	740	.897	.103	.262	.738	745	.260	.74
1000	740	.777	.223	.189	.811	742	.185	.815
1500	740	.655	.345	.17	.830	736	.168	.832
2000	740	.523	.477	.197	.803	812	.393	.607
2130	740	.472	.528	.232	.768	613	.061	.939
2180	740	.444	.556	.249	.751	588	.050	.950
2222	740	.402	.598	.275	.725	560	.04	.96
500	800	.921	.079	.478	.522	801	.454	.546
1000	800	.792	.208	.346	.654	771	.248	.752
1500	800	.637	.363	.34	.660	683	.098	.902
1575	800	.612	.388	.342	.658	658	.077	.923
1633	800	.578	.422	.359	.641	606	.044	.956

TABLE C3

Comparison of the Temperature and Vapor Composition Calculated by Chueh-Prausnitz Method with the Experimental Values for the Nitrogen-Methane-n-Hexane Ternary (8)

E X P E R I M E N T A L				P R E D I C T E D				
P (PSIA)	T (°R)	X, Mole Fraction		Y, Mole Fraction		T (°R)	Y, Mole Fraction	
		n-C ₆	C ₁ N ₂	n-C ₆	C ₁ N ₂		n-C ₆	C ₁ N ₂
532	537	.839	.159 .002	.033	.897 .07	571	.022	.948 .030
532	537	.835	.162 .003	.026	.92 .054	559	.018	.938 .043
1000	537	.713	.278 .009	.018	.934 .048	562	.019	.914 .067
1485	537	.596	.392 .012	.021	.909 .07	565	.024	.919 .057
1485	537	.597	.390 .013	.021	.916 .063	565	.024	.914 .062
1980	537	.494	.485 .021	.03	.888 .082	569	.035	.895 .070
2465	537	.392	.578 .03	.046	.883 .071	564	.044	.882 .074
2465	537	.39	.583 .027	.047	.896 .057	565	.046	.888 .066
2970	537	.279	.69 .031	.881	.844 .075	540	.050	.894 .056
2970	537	.274	.689 .037	.082	.838 .08	537	.048	.886 .066
3060	537	.237	.734 .029	.105	.838 .057	523	.045	.908 .047
3060	537	.236	.726 .038	.104	.833 .063	522	.043	.896 .061
3360	537	.18	.771 .049	.175	.779 .046	499	.035	.898 .068
532	591	.855	.142 .003	.049	.873 .078	608	.043	.911 .046
1485	591	.628	.355 .017	.034	.899 .067	596	.035	.879 .086
2465	591	.421	.553 .026	.057	.882 .06	591	.058	.875 .067
2970	591	.303	.662 .035	.109	.827 .064	550	.054	.880 .066
2970	591	.306	.654 .040	.109	.828 .063	550	.054	.870 .076
3060	591	.249	.71 .041	.146	.808 .046	527	.045	.887 .068
3060	591	.250	.715 .035	.145	.808 .047	528	.046	.896 .058
3220	591	.189	.768 .043	.186	.768 .046	503	.036	.903 .061

TABLE C4

Comparison of the Temperature and Vapor Composition Calculated by Chueh-Prausnitz Method with the Experimental Values for the Nitrogen-Methane-n-Hexane Ternary (43)

E X P E R I M E N T A L				P R E D I C T E D				
P (PSIA)	T (°R)	X, Mole Fraction		Y, Mole Fraction		T (°R)	Y, Mole Fraction	
		n-C ₆	C ₁ N ₂	n-C ₆	C ₁ N ₂			
500	560	.870	.109 .021	.017	.609 .374	553	.016	.665 .319
1000	560	.876	.044 .080	.018	.307 .675	808	.360	.166 .474
1000	560	.727	.264 .009	.020	.909 .071	579	.024	.902 .073
1500	560	.804	.083 .113	.011	.202 .787	806	.543	.166 .291
1500	560	.772	.131 .097	.013	.302 .685	796	.337	.325 .338
1500	560	.754	.162 .084	.013	.884 .603	787	.299	.403 .298
1500	560	.614	.370 .016	.022	.912 .066	582	.030	.891 .079
2000	560	.598	.323 .079	.022	.616 .362	600	.043	.652 .305
2000	560	.589	.337 .075	.017	.648 .335	595	.041	.673 .286
2000	560	.519	.460 .021	.021	.913 .066	602	.049	.880 .071
2000	560	.666	.229 .105	.014	.408 .578	796	.389	.395 .216
2500	560	.449	.489 .062	.020	.756 .224	582	.051	.783 .116
2500	560	.512	.389 .099	.017	.607 .376	593	.051	.654 .295
2500	560	.614	.24 .146	.019	.401 .580	798	.382	.370 .248
3000	560	.629	.171 .199	.019	.241 .740	756	.325	.274 .4
3000	560	.659	.139 .202	.019	.2	768	.363	.227 .410
3000	560	.691	.093 .216	.014	.134 .852	765	.381	.157 .462
3000	560	.342	.587 .071	.020	.820 .160	558	.055	.801 .144
3500	560	.443	.397 .160	.027	.523 .450	591	.077	.563 .360
3500	560	.457	.378 .165	.030	.536 .434	596	.081	.542 .377

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